Supporting Information

Synthesis of Axially Chiral Thiourea by NHC-Catalyzed Desymmetrizative Amidation

Yingtao Wu [a], Xin Guan [a], Kehan Jiao [b], Huaqiu Zhao [a], Mingrui Li [a], Jiaqiong Sun [b], Guangfan Zheng*[,a] and Qian Zhang[a,c]

[a] Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, Department of Chemistry, Northeast Normal University, Changchun 130024, China

E-mail: zhenggf265@nenu.edu.cn

[b] School of Environment, Northeast Normal University, Changchun 130117, China

[c] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences 345 Lingling Lu, Shanghai 200032, China

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I. General Information.

All reactions were performed under nitrogen atmosphere in flame dried flasks. All reactions were monitored by thin layer chromatography (TLC) using Macherey-Nagel 0.20 mm silica gel 60 plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Taizhou, China). ^{1}H, ^{13}C, ^{19}F spectra were recorded with Varian 500 MHz (Inova-500) or Bruker 600 MHz (Avance-600) instrument. Chemical shifts were referenced to δ_{TMS} = 0.00 ppm (^{1}H, ^{13}C). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Dichloromethane-d_2 (δ (^{1}H) = 5.32 ppm, δ (^{13}C) = 53.8 ppm), chloroform-d_1 (δ (^{1}H) = 7.26 ppm, δ (^{13}C) = 77.2 ppm) or methanol-d_4 (δ (^{1}H) = 3.31 ppm, δ (^{13}C) = 49.0 ppm) were used as solvents. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = triplet of doublet, td = doublet of triplet, bs = broad singlet. High-pressure liquid chromatography (HPLC) was performed on Agilent 1200 Series chromatographs using a chiral column (25 cm) as noted for each compound. High-resolution mass spectra HRMS (ESI-TOF) were recorded on Brucker microtof. Compounds were visualized by irradiation with UV light, or stained with iodine/silica gel, or potassium permanganate. Preparatory thin-layer chromatography (Prep-TLC) was performed on silica gel GF with UV 254 (20 × 20 cm, 1000 microns, from Yantai Jiang you Silica Gel Development Co., Ltd.) and visualized with UV light. Optical rotations were reported as follows: $[\alpha]_D^{T}$ = (c: g/100 mL in CH_2Cl_2).

II. Experimental Section

2.1 Synthesis of Starting Materials

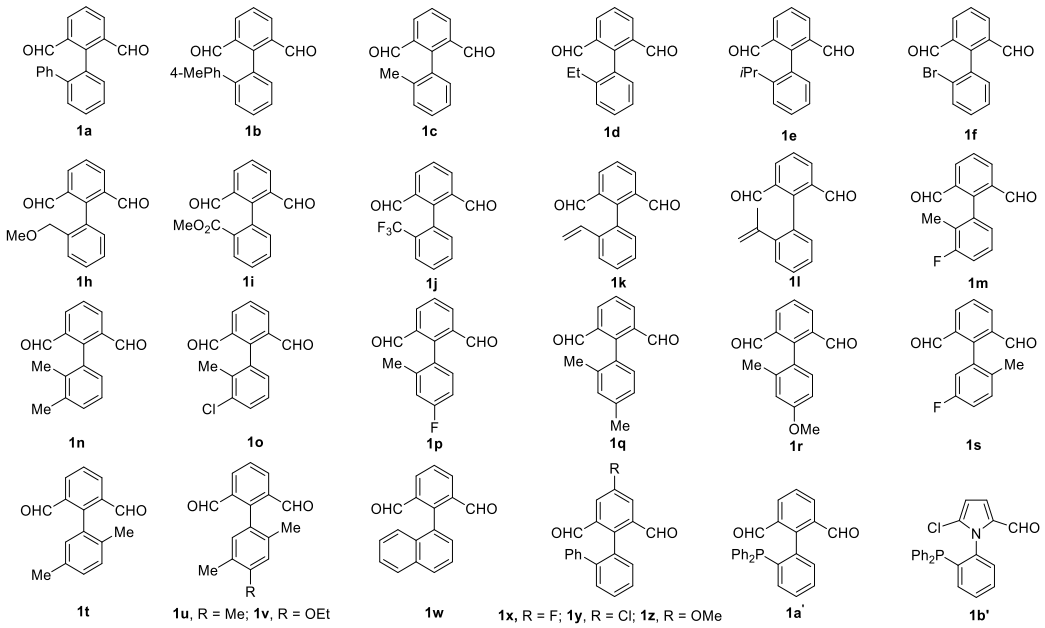
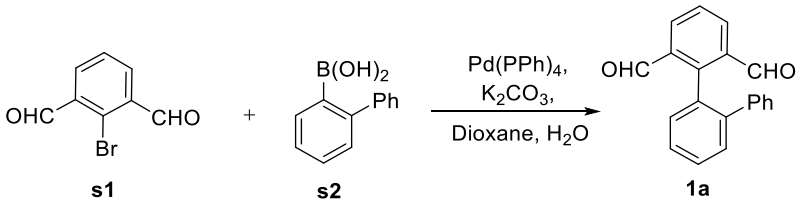


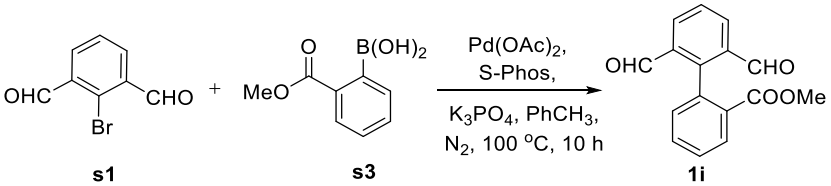
Figure S1. List of starting materials

2.1.1 General procedure for the synthesis of Substrates 1a-h and 1j-w.[1] Preparation of 1a is shown as a representative example.



A 250 mL round-bottom Schlenk flask was charged with 2-bromoisophthalaldehyde (2.13 g, 10.0 mmol), 2-biphenylboronic acid (4.536 g, 22.9 mmol), K_2CO_3 (9.59 g, 68.9 mmol) and $Pd(PPh_3)_4$ (0.21 g, 0.18 mmol) and was evacuated and charged with argon three times. Then degassed 1,4-dioxane (112 mL) and water (15 mL) were added and the reaction was heated at 95 °C for 3 days under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : cyclohexane = 1:20 to 1:10) and washed with ethanol to give compound as a white solid (2.3 g, yield: 81 %).

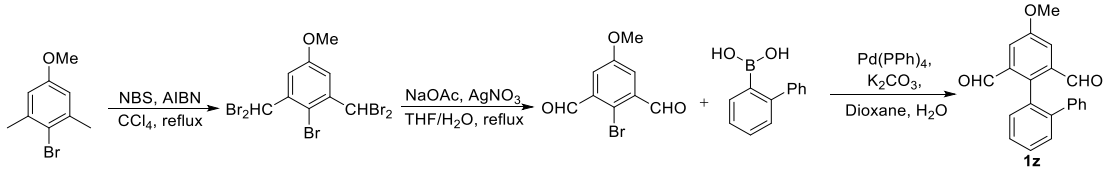
2.1.2 Procedure for the synthesis of Substrates 1i.



A 25 mL round-bottom Schlenk flask was charged with 2-bromoisophthalaldehyde **s1** (0.639 g, 3.0

mmol), 2-methoxycarbonylphenylboronic acid **s3** (1.35 g, 2,5 equiv), S-Phos (0.124 g, 10 mol%), K_3PO_4 (3.82 g, 6.0 equiv) and $Pd(OAc)_2$ (0.034 g, 5 mol%) and was evacuated and charged with argon three times. Then degassed toluene (12 mL) were added and the reaction was heated at 100 °C for 10 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : cyclohexane = 1:20 to 1:10) and washed with ethanol to give compound as a white solid (0.57 g, yield: 71 %).

2.1.3 General procedure for the synthesis of Substrates 1x-z.[2b] Preparation of 1z is shown as a representative example.

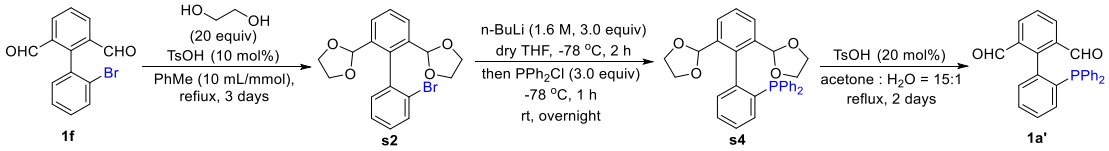


2-bromo-5-methoxy-1,3-dimethylbenzene (5 mmol), NBS (4.5 equiv.) and AIBN (50 mol%) cat. were dissolved in CCl_4 (50 mL) and refluxed for 16 h, The mixture was cooled and the precipitated succinimide was removed by filtration. The solvent was removed under reduced pressure to give a brown oil which was purified by flash column chromatography (petroleum ether) to give the corresponding brominated compound (69% yield);

2-bromo-1,3-bis(dibromomethyl)-5-methoxybenzene (3.4 mmol), sodium acetate (8.5 equiv.) and silver nitrate (16.1 equiv.) were dissolved in a mixture of THF and H_2O (5:1). The mixture was heated at reflux for 24 h. The inorganic precipitate was filtered, washed, and the solvent was removed in vacuo. The crude mixture was purified by flash column chromatography (ethyl acetate : petroleum ether = 1:10 to 1:20) to give the 2-bromo-5-methoxyisophthalaldehyde (92% yield);

2-bromo-5-methoxyisophthalaldehyde (3.1 mmol), 2-biphenylboronic acid (2.29 equiv), K_2CO_3 (9.59 g, 6.89 equiv) and $Pd(PPh_3)_4$ (0.018 mmol) and was evacuated and charged with argon three times. Then degassed 1,4-dioxane (33 mL) and water (5 mL) were added and the reaction was heated at 95 °C for 3 days under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : petroleum ether = 1:20 to 1:10) and washed with ethanol to give compound as a light yellow solid (0.5 g, yield: 51 %).

2.1.4 Procedure for the synthesis of Substrates 1a'.



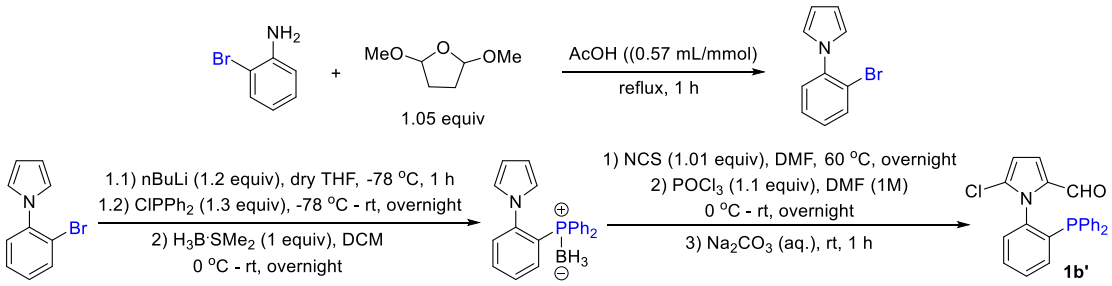
To a solution of 5-bromoisatin (1.44 g, 5 mmol) in toluene (50 mL), ethylene glyco1 (5.6 mL, 100 mmol) and p-toluenesulphonic acid (86.1 mg, 0.5 mmol) were added. The reaction mixture was refluxed for 3 days and then evaporated to dryness. The residue was diluted with dichlomethane and washed with saturated sodium bicarbonate solution. The aqueous layer was extracted with dichloromethane three times. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and evaporated. The crude mixture was purified using column chromatography to

give the product **s2**. Yie1d: 55%.

To a distilled THF solution (14 mL) of **s2** (2.75 mmol) was added dropwise nBuLi (5.2 mL, 8.25 mmol, 1.6 M in hexane) at -78 °C under N_2 atmosphere. The reaction mixture was stirred for 2 hour, then Ph_2PCl (8.25 mmol) was added at -78 °C, then the temperature was slowly raised to room temperature and stirred overnight, The reaction mixture was quenched with saturated aqueous ammonium chloride solution and extracted using ethyl acetate. The organic extracts were combined dried over with anhydrous sodium sulphate and concentrated in vacuo, the residual viscous crude product was purified by silica gel chromatography using petroleum ether/ethyl acetate 20:1-10:1 (v/v) to give the product **s4** (yield: 10%, 0.24 mmol).

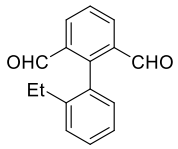
s4 was dissolved in acetone/water (2 mL, 15:1) mixture in a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar, TsOH (20% mmol) was added and stirred at 60 ºC for 2 days. The reaction mixture was quenched with saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extracts were combined, dried over anhydrous sodium sulphate and concentrated. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (5:1) as eluent to afford compounds **1a'** (yield: 50%, 0.12 mmol).

2.1.5 Procedure for the synthesis of Substrates 1b'.[3]



2.1.6 Characterization data of the substrates

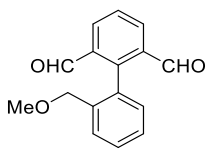
2'-ethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1d

1d: light green solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.71 (d, *J* = 0.8 Hz, 2H), 8.27 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.41 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.33 (td, *J* = 7.5, 1.3 Hz, 1H), 7.22 (dd, *J* = 7.5, 1.3 Hz, 1H), 2.36 (q, *J* = 7.6 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.05, 147.88, 143.01, 134.91, 132.71, 131.71, 130.86, 129.74, 128.85, 128.64, 126.09, 26.72, 14.73. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NaO_2$, ([M + Na]$^+$), 261.0886; found 261.0882.

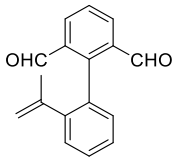
2'-(methoxymethyl)-[1,1'-biphenyl]-2,6-dicarbaldehyde



1h

1h: white solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.64 (d, *J* = 1.0 Hz, 2H), 8.26 (d, *J* = 7.7 Hz, 2H), 7.68 (td, *J* = 7.8, 1.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.49 – 7.44 (m, 1H), 7.34 – 7.28 (m, 1H), 4.06 (s, 2H), 3.06 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.55, 146.24, 136.95, 134.86, 132.96, 132.16, 130.82, 129.70, 129.36, 128.64, 128.15, 72.85, 58.05. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NaO_3$, ([M + Na]$^+$), 277.0835; found 277.0827.

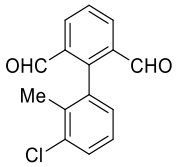
2'-(prop-1-en-2-yl)-[1,1'-biphenyl]-2,6-dicarbaldehyde



1l

1l: white solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.76 (s, 2H), 8.24 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.50 (td, *J* = 7.6, 1.4 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.30 – 7.22 (m, 1H), 5.02 (t, *J* = 1.6 Hz, 1H), 4.82 (s, 1H), 1.56 (t, *J* = 1.2 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.84, 147.74, 144.63, 144.47, 134.62, 132.54, 131.45, 129.89, 129.54, 128.82, 128.47, 127.22, 118.41, 23.24. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{14}NaO_2$, ([M + Na]$^+$), 273.0886; found 273.0887.

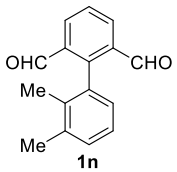
3'-chloro-2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1o

1o: white solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.71 (s, 2H), 8.28 (d, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 2.11 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.29, 146.75, 135.90, 134.51, 134.27, 132.98, 130.25, 129.14, 128.91, 126.81, 117.13, 17.99. **HRMS**(ESI-TOF) (m/z): Calcd for $C_{15}H_{11}ClNaO_2$, ([M + Na]$^+$), 281.0340; found 281.0341.

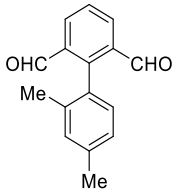
2'-ethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1n

1n: white solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.70 (s, 2H), 8.26 (d, *J* = 7.7 Hz, 2H), 7.66 (s, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 1.97 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.01, 148.69, 137.71, 135.48, 134.71, 132.52, 132.17, 130.75, 128.57, 128.29, 125.55, 20.40, 17.10. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NaO_2$, ([M + Na]$^+$), 261.0886; found 261.0882.

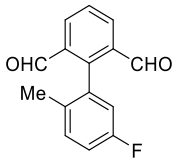
2',4'-dimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1q

1q: white solid; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.79 (s, 2H), 8.32 (d, *J* = 7.7 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 7.23 – 7.20 (m, 2H), 2.49 (s, 3H), 2.10 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.88, 148.05, 139.14, 136.59, 134.78, 132.55, 131.08, 130.63, 129.14, 128.31, 126.73, 21.18, 20.29. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NaO_2$, ([M + Na]$^+$), 261.0886; found 261.0887.

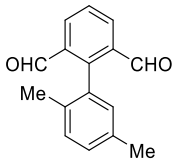
5'-fluoro-2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1s

1s: light yellow solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.72 (d, *J* = 0.9 Hz, 2H), 8.28 (d, *J* = 7.7 Hz, 2H), 7.70 (td, *J* = 7.8, 0.9 Hz, 1H), 7.33 (dd, *J* = 8.6, 5.6 Hz, 1H), 7.14 (td, *J* = 8.4, 2.7 Hz, 1H), 7.00 (dd, *J* = 8.6, 2.8 Hz, 1H), 2.01 (s, 3H).**^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.30, 160.78 (*J* = 246.8 Hz), 146.30, 134.35, 134.98 (*J* = 7.1 Hz), 132.99, 132.65 (*J* = 4.3 Hz), 131.89 (*J* = 7.9 Hz), 128.95, 117.45 (*J* = 21.9 Hz), 116.29 (*J* = 20.7 Hz), 19.60. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -116.43 – -116.47. (m, 1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{15}H_{11}FNaO_2$, ([M + Na]$^+$), 265.0635; found 265.0635.

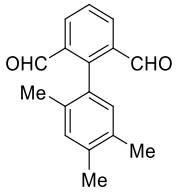
2',5'-dimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1t

1t: light yellow solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.71 (s, 2H), 8.26 (d, *J* = 7.7 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.05 (s, 1H), 2.36 (s, 3H), 2.01 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ191.07, 148.27, 135.65, 134.57, 133.69, 132.56, 131.95, 131.30, 130.21, 130.07, 128.35, 20.87, 19.88. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{16}H_{14}NaO_2$, ([M + Na]$^+$), 261.0886; found 261.0894.

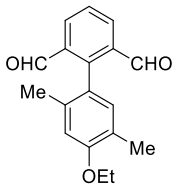
2',4',5'-trimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1u

1u: white solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.72 (d, *J* = 0.9 Hz, 2H), 8.24 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.11 (s, 1H), 6.98 (s, 1H), 2.32 (s, 3H), 2.26 (s, 3H), 1.98 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ191.29, 148.39, 137.78, 134.74, 134.24, 133.97, 132.48, 131.89, 131.56, 129.26, 128.19, 19.75, 19.49, 19.21. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{17}H_{16}NaO_2$, ([M + Na]$^+$), 275.1043; found 275.1038.

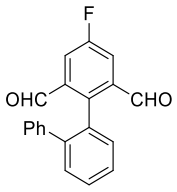
4'-ethoxy-2',5'-dimethyl-[1,1'-biphenyl]-2,6-dicarbaldehyde



1v

1v: light green solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.74 (d, *J* = 0.9 Hz, 2H), 8.23 (d, *J* = 7.7 Hz, 2H), 7.63 (dd, *J* = 8.2, 7.2 Hz, 1H), 6.98 (s, 1H), 6.76 (s, 1H), 4.10 (d, *J* = 7.0 Hz, 2H), 2.22 (s, 3H), 2.00 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ191.45, 157.72, 148.40, 135.32, 135.05, 132.80, 132.47, 128.12, 124.59, 123.11, 112.50, 63.69, 20.45, 15.75, 14.92. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{18}H_{18}NaO_3$, ([M + Na]$^+$), 305.1148; found 305.1168.

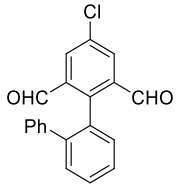
4-fluoro-[1,1':2',1''-terphenyl]-2,6-dicarbaldehyde



1x

1x: white solid; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.78 (d, *J* = 3.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.63 (td, *J* = 7.6, 1.4 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.39 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.19 – 7.17 (m, 3H), 6.95 (dd, *J* = 6.7, 2.9 Hz, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 189.23, 162.17 (*J* = 250.4 Hz), 143.36 (*J* = 3.5 Hz), 143.08, 139.39, 136.86 (*J* = 5.7 Hz), 132.04, 130.47, 130.24, 129.98, 129.33, 128.52, 127.55 (*J* = 13.8 Hz), 119.06, 118.91. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -110.76. (s,1F). **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{13}FNaO_2$, ([M + Na]$^+$), 327.0792; found 327.0788.

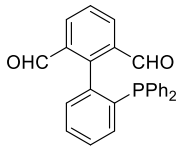
4-chloro-[1,1':2',1''-terphenyl]-2,6-dicarbaldehyde



1y

1y: white solid; **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 9.77 (s, 2H), 8.03 (s, 2H), 7.63 (td, *J* = 7.6, 1.4 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.38 – 7.36 (m, 1H), 7.19 – 7.18 (m, 3H), 6.97 – 6.95 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ189.18, 145.44, 142.90, 139.30, 136.05, 135.32, 132.13, 131.85, 130.51, 130.09, 130.06, 129.33, 128.58, 127.62, 127.57. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{20}H_{13}ClNaO_2$, ([M + Na]$^+$), 343.0496; found 343.0498.

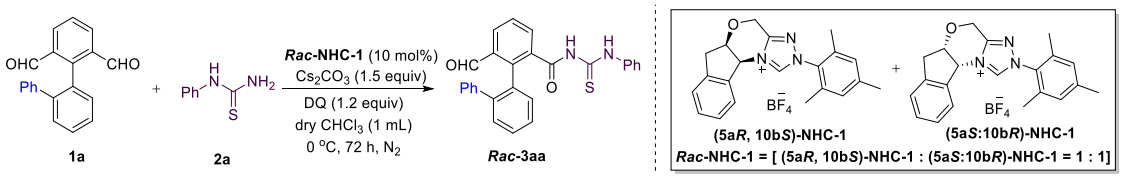
2'-(diphenylphosphanyl)-[1,1'-biphenyl]-2,6-dicarbaldehyde



1a'

1a': white solid; **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 9.50 (s, 2H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.33 – 7.26 (m, 7H), 7.18 – 7.13 (m, 5H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.07, 146.66 (d, *J* = 6.7 Hz), 139.38 (d, *J* = 14.0 Hz), 137.68 (d, *J* = 28.2 Hz), 134.37, 134.33 (d, *J* = 20.1 Hz), 134.14 (d, *J* = 10.3 Hz), 132.83, 132.12, 131.46 (d, *J* = 4.6 Hz), 129.41, 129.30, 128.72, 128.67, 128.62. **^{31}P NMR (243 MHz, Chloroform-*d*)** δ -11.63. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{26}H_{19}NaO_2P$, ([M + Na]$^+$), 417.1015; found 417.1005.

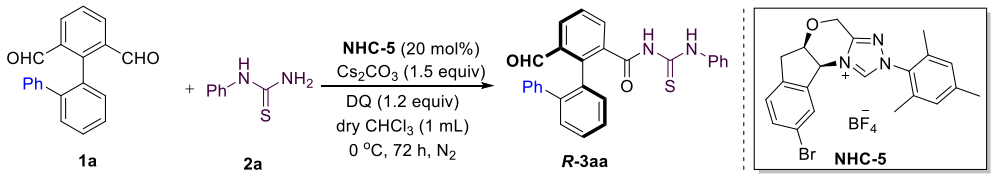
2.2 General Synthetic Procedure of 3.



Racemic Synthesis:

Preparation of ***Rac*-NHC-1**: **(5a*R*, 10b*S*)-NHC-1** (100 mg) and **(5a*S*, 10b*R*)-NHC-1** (100 mg) are completely dissolved in dry DCM and concentrated to remove DCM.

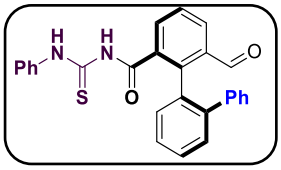
Representative Synthesis of Product (*Rac*)-3aa. In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with ***Rac*-NHC-1** (10 mol%, 4.18 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), [1,1':2',1"-terphenyl]-2,6-dicarbaldehyde **1a** (0.1 mmol, 29 mg) and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (46.0 mg, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the racemic product *Rac*-**3aa**.



Asymmetric Synthesis:

Representative Synthesis of Product *R*-3aa (standard conditions A): In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **(5a*R*, 10b*S*)-NHC-5** (20 mol%, 10.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), [1,1':2',1"-terphenyl]-2,6-dicarbaldehyde **1a** (0.1 mmol, 29 mg) and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (46.0 mg, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product ***R*-3aa**.

(*R*)-6-formyl-*N*-(phenylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3aa)

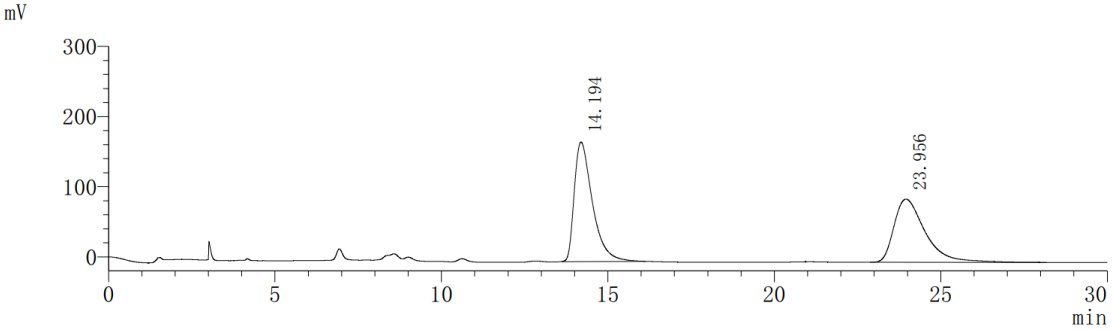


The title compound **3aa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10: 3). **3aa** was obtained as a light yellow solid (33.6 mg, 77%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.05 (s, 1H), 9.86 (s, 1H), 8.31 (s, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.63 – 7.53 (m, 6H), 7.41 – 7.38 (m, 3H), 7.28 – 7.18 (m, 4H), 7.08 – 7.06 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.98, 177.82, 167.31, 143.91, 142.04, 139.52, 137.63, 135.55, 134.31, 133.33, 132.33, 131.45, 131.40, 131.13, 130.36, 129.57, 129.05, 128.60, 128.49, 128.27, 127.80, 127.06, 124.14.

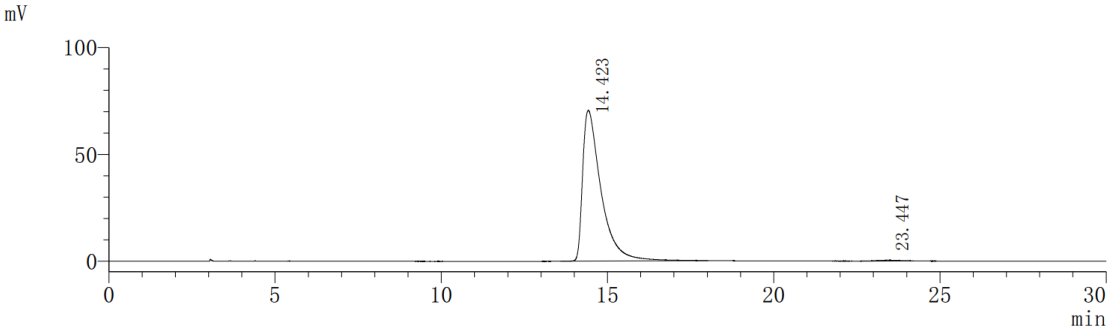
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{21}N_2O_2S$, ([M + H]$^+$), 437.1318; found 437.1314.

[α]$_D^{20}$ = -77.3 (c = 1.7, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 14,42 min, t_R (minor) = 23.35 min, 99% ee.

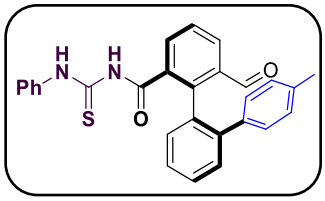


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.194	M	0.9798	6451325	170382	52.3775
2	23.956	M	1.6375	5865661	90150	47.6225



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.423	M	0.9629	2721001	70651	99.2210
2	23.447	M	1.4515	21363	401	0.7790

(*R*)-6-formyl-4''-methyl-*N*-(phenylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ba)

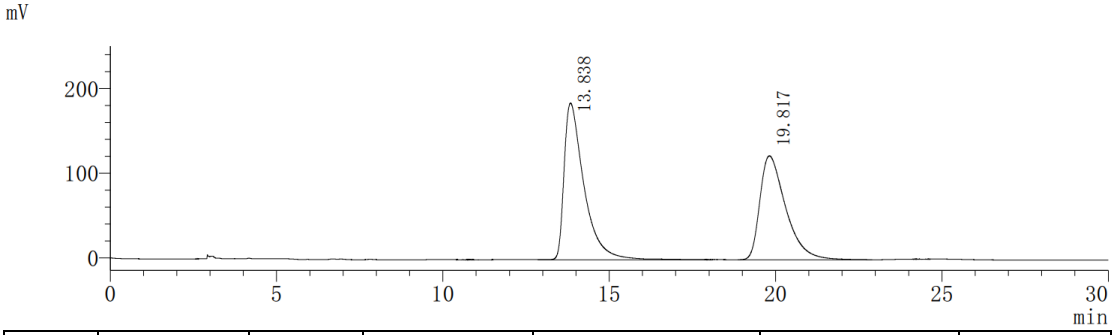


The title compound **3ba** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10: 3). **3ba** was obtained as a light yellow oil (38.3 mg, 85%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.02 (s, 1H), 9.87 (s, 1H), 8.17 (s, 1H), 8.14 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.79 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.63 – 7.51 (m, 6H), 7.41 – 7.35 (m, 3H), 7.28 – 7.25 (m, 1H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.12, 177.96, 167.32, 144.21, 141.88, 137.67, 137.65, 136.52, 135.64, 134.41, 133.06, 132.23, 131.57, 131.41, 131.07, 130.27, 129.46, 129.41, 129.03, 128.36, 127.95, 127.02, 124.17, 21.33.

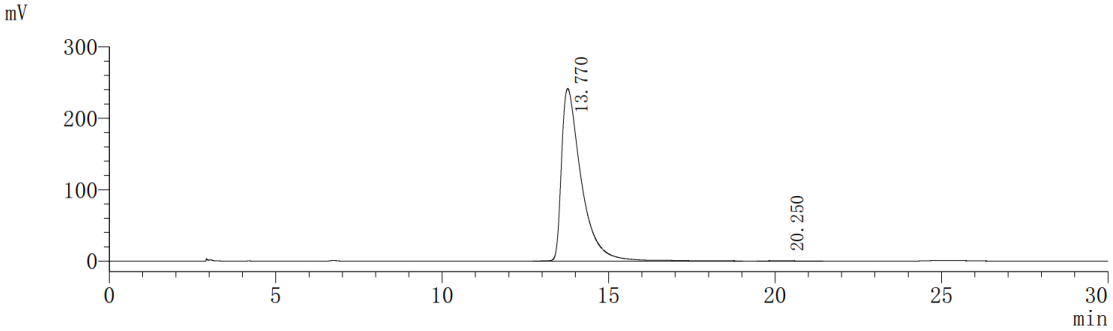
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{23}N_2O_2S$, ($[M + H]^+$), 451.1475; found 451.1469.

$[\alpha]_D^{20}$ = -78.1 (c = 1.9, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 13.77 min, t_R (minor) = 20.25 min, 99% ee.

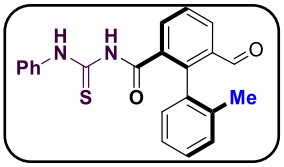


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.838	SV	1.0411	7703834	185027	53.7366
2	19.817	M	1.3948	6632449	122769	46.2634



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.770	SV	1.0255	10000283	241582	99.9027
2	20.250	M	1.1103	9740	211	0.0973

(*R*)-6-formyl-2'-methyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3ca)

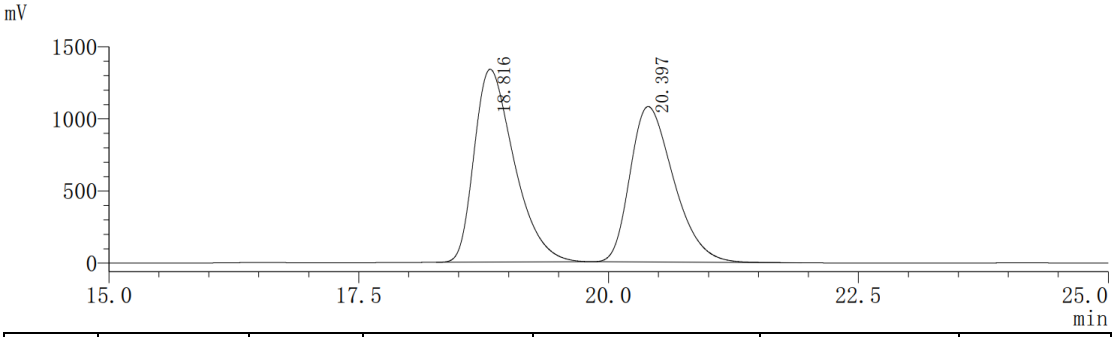


The title compound **3ca** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10: 3). **3ca** was obtained as a yellow oil (20.9 mg, 56%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.14 (s, 1H), 9.63 (s, 1H), 8.57 (s, 1H), 8.23 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.14 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.45 (td, *J* = 7.5, 1.4 Hz, 1H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.39 (td, *J* = 7.3, 1.4 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 2.14 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.01, 177.59, 167.19, 143.30, 137.56, 136.64, 134.94, 134.39, 133.90, 133.28, 131.39, 131.29, 130.19, 129.75, 128.96, 128.85, 127.13, 126.98, 124.03, 20.37.

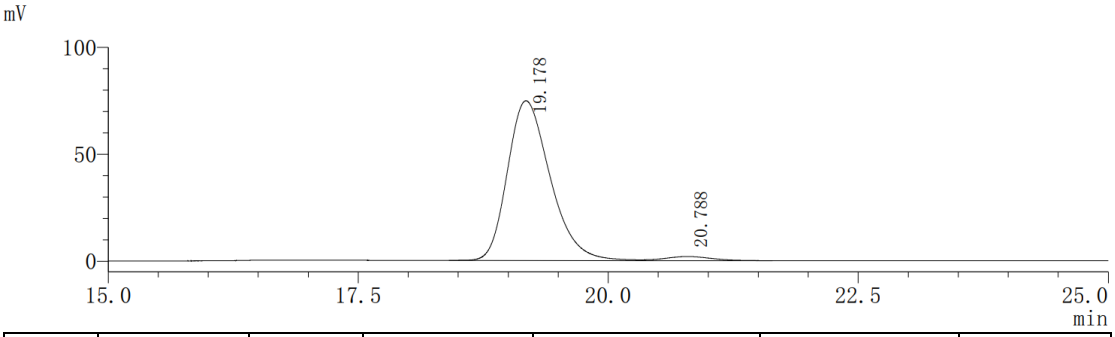
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{19}N_2O_2S$, ($[M + H]^+$), 375.1162; found 375.1151.

$[\alpha]_D^{20}$ = -37.2 (c = 1.0, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IC-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 19.18 min, t_R (minor) = 20.79 min, 95% ee.

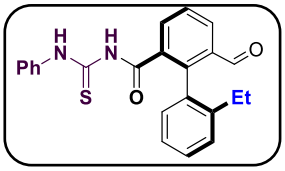


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	18.816	M	0.7265	37264452	1337010	53.2226
2	20.397	M	0.7983	32751813	1077898	46.7774



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	19.178	M	0.7736	2225705	74734	97.2718
2	20.788	M	0.8701	62426	1936	2.7282

(*R*)-2'-ethyl-6-formyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3da)

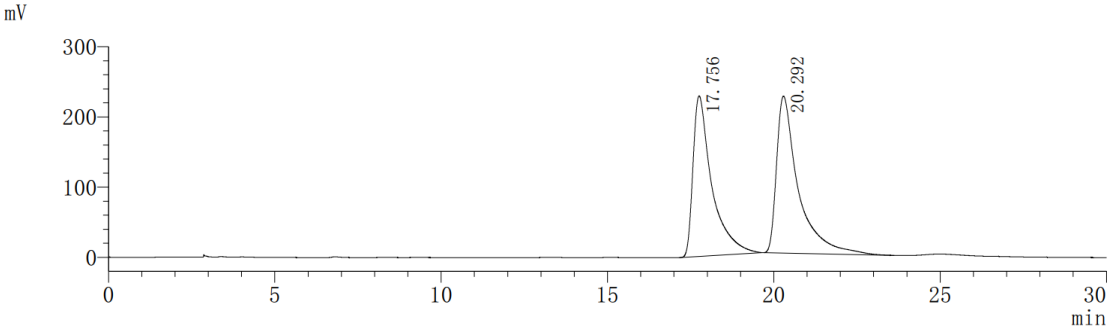


The title compound **3da** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10: 3). **3da** was obtained as a yellow oil (27.6 mg, 71%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.17 (s, 1H), 9.64 (d, *J* = 0.9 Hz, 1H), 8.50 (s, 1H), 8.24 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.70 (td, *J* = 7.8, 0.9 Hz, 1H), 7.61 – 7.59 (m, 2H), 7.54 – 7.48 (m, 2H), 7.41 (td, *J* = 7.3, 1.8 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.26 – 7.22 (m, 2H), 2.51 – 2.36 (m, 2H), 1.11 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.08, 177.52, 167.07, 143.09, 142.50, 137.58, 135.12, 134.63, 133.79, 132.56, 131.32, 130.53, 129.84, 129.79, 128.98, 128.89, 127.18, 126.97, 124.04, 26.51, 14.60.

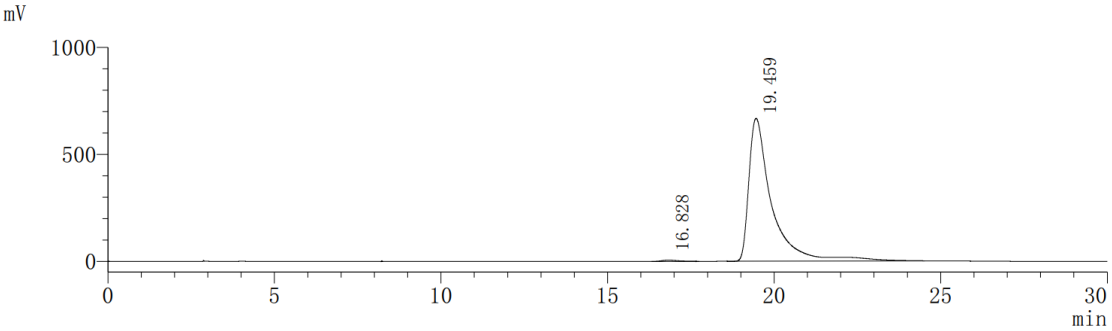
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{21}N_2O_2S$, ($[M + H]^+$), 389.1318; found 389.1318.

$[\alpha]_D^{20}$ = -27.6 (c = 1.4, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 16.83 min, t_R (major) = 19.46 min, 99% ee.

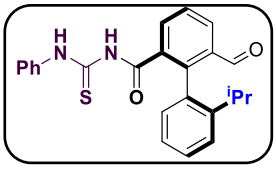


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	17.756	M	0.9061	8994700	228629	46.9218
2	20.292	M	1.0193	10174857	223670	53.0782



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	16.828	M	0.8227	205703	6335	0.6388
2	19.459	M	1.0358	31995610	668226	99.3612

(*R*)-6-formyl-2'-isopropyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3ea)

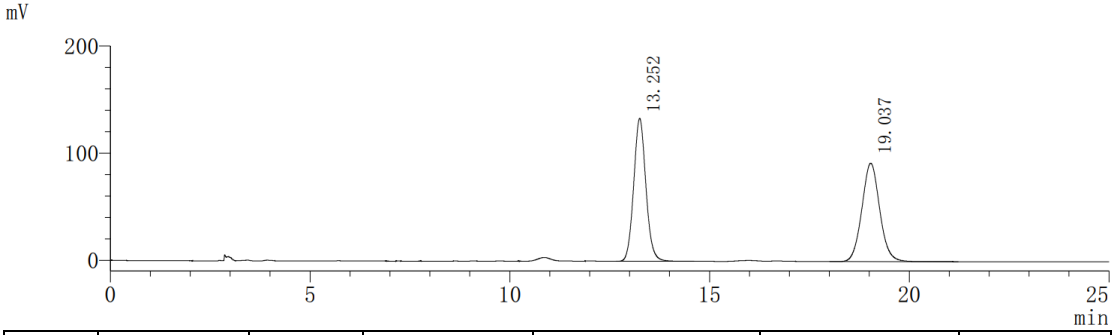


The title compound **3ea** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10: 3). **3ea** was obtained as a light yellow oil (24.1 mg, 60%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.18 (s, 1H), 9.65 (s, 1H), 8.57 (s, 1H), 8.24 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.17 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.59 – 7.58 (m, 2H), 7.55 (d, *J* = 4.3 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.25 – 7.22 (m, 2H), 2.65 – 2.58 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.00, 177.62, 167.07, 147.62, 143.26, 137.60, 135.37, 134.53, 133.83, 131.79, 131.36, 130.79, 129.75, 128.98, 128.81, 127.29, 127.02, 126.99, 124.13, 30.73, 24.39, 23.51.

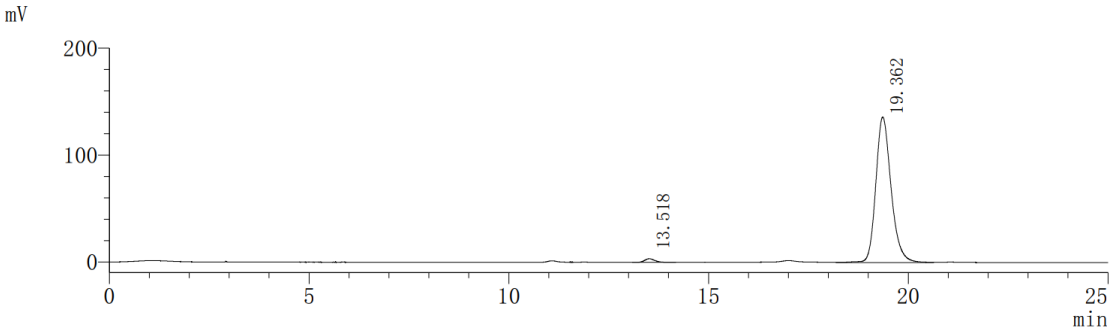
HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{23}N_2O_2S$, ($[M + H]^+$), 403.1475; found 403.1467.

$[\alpha]_D^{20}$ = -68.8 (c = 1.2, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 13.52 min, t_R (major) = 19.36 min, 97% ee.

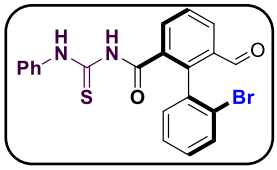


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.252	M	0.5533	2835695	133311	49.7426
2	19.037	M	0.8109	2865041	91939	50.2574



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.518	M	0.4544	61974	3432	1.6819
2	19.362	M	0.6810	3622790	136127	98.3181

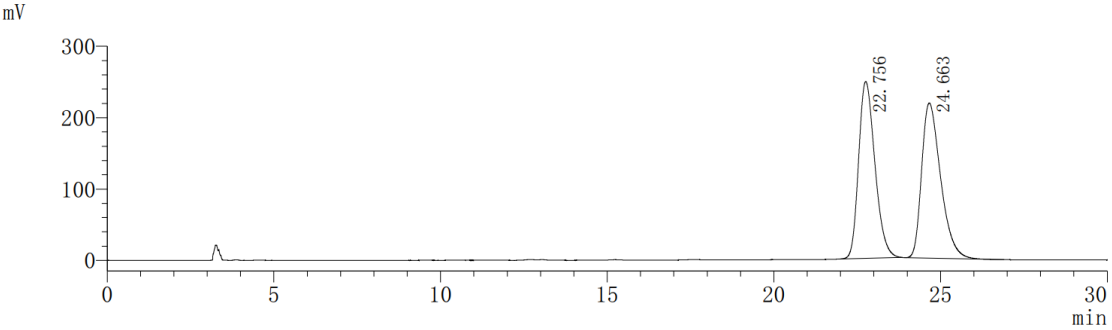
(*R*)-2'-bromo-6-formyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3fa)



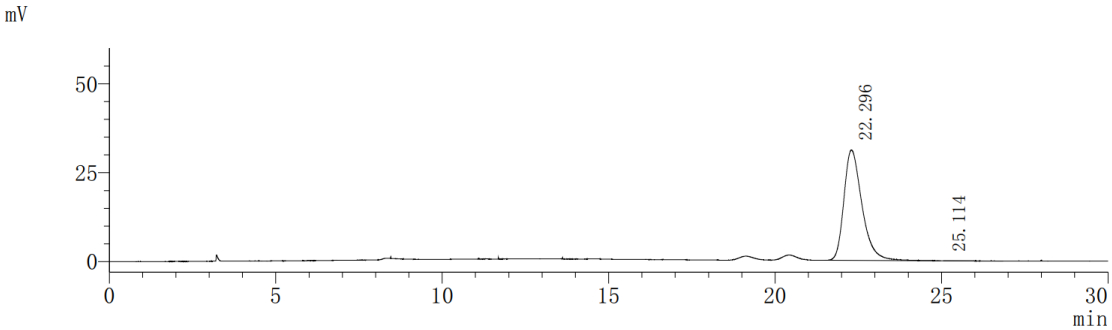
The title compound **3fa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10: 3). **3fa** was obtained as a yellow oil (20.6 mg, 47%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.03 (s, 1H), 9.68 (d, *J* = 0.8 Hz, 1H), 8.63 (s, 1H), 8.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.04 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.80 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.73 (td, *J* = 7.7, 0.8 Hz, 1H), 7.61 – 7.60 (m, 2H), 7.51 (td, *J* = 7.5, 1.2 Hz, 1H), 7.41 (td, *J* = 7.8, 1.7 Hz, 1H), 7.38 – 7.35 (m, 3H), 7.26 – 7.23 (m, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.30, 177.58, 167.18, 142.34, 137.53, 135.23, 134.82, 134.47, 133.65, 133.54, 131.44, 131.39, 131.32, 129.50, 129.02, 128.36, 127.08, 124.08, 123.94. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{21}H_{16}BrN_2O_2S$, ([M + H]$^+$), 439.0110; found 439.0108.

[α]$_D^{20}$ = -7.0 (c = 1.0, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IC-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 22.30 min, t_R (major) = 25.11 min, 99% ee.

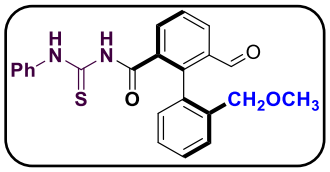


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	22.756	M	0.8898	8416453	247943	49.4297
2	24.663	M	1.0335	8610652	217373	50.5703



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	22.296	M	0.9660	1173257	31043	99.9816
2	25.114	M	0.0256	216	14	0.0184

(*R*)-6-formyl-2'-(methoxymethyl)-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3ha)

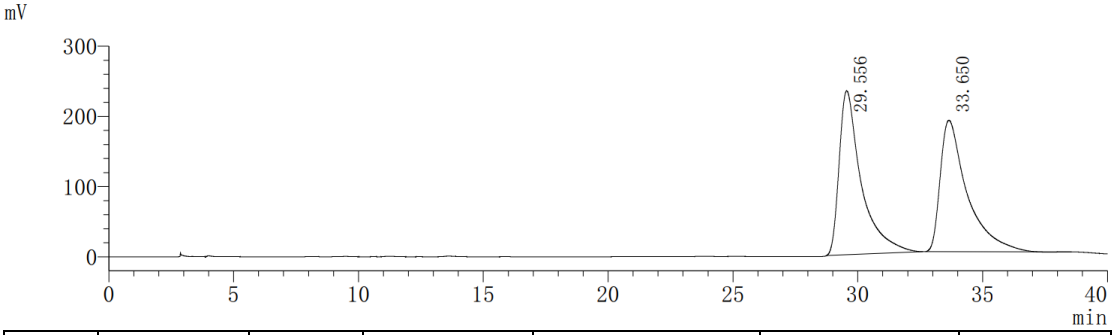


The title compound **3ha** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10: 3). **3ha** was obtained as a yellow oil (29.9 mg, 74%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.21 (s, 1H), 10.17 (s, 1H), 9.65 (s, 1H), 8.18 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.97 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.52 – 7.46 (m, 3H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 4.3 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 4.37 (d, *J* = 10.4 Hz, 1H), 4.28 (d, *J* = 10.4 Hz, 1H), 3.10 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.01, 178.10, 168.78, 141.47, 137.79, 136.19, 135.74, 134.48, 134.08, 133.41, 130.54, 130.08, 130.04, 129.81, 129.62, 128.89, 128.83, 126.70, 124.06, 74.04, 58.89.

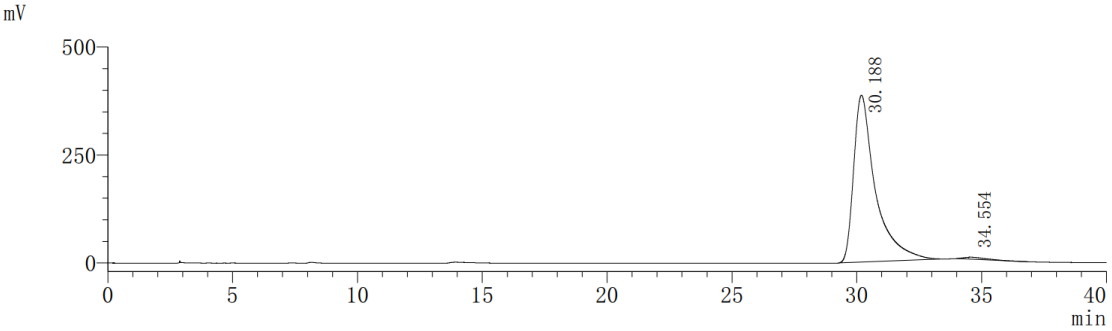
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{21}N_2O_3S$, ($[M + H]^+$), 405.1267; found 405.1272.

$[\alpha]_D^{20}$ = 107.6 (c = 1.5, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 30.19 min, t_R (minor) = 34.55 min, 97% ee.

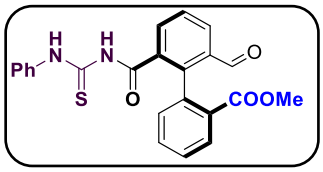


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	29.556	M	1.4748	14386839	233539	50.7037
2	33.650	M	1.8154	13987507	187129	49.2963



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	30.188	M	1.3999	23420960	386337	98.7445
2	34.554	M	1.8948	297790	4743	1.2555

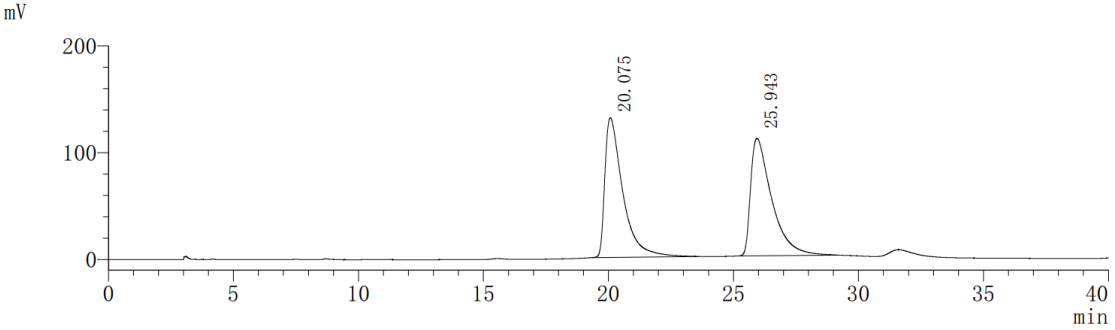
methyl (*R*)-2'-formyl-6'-((phenylcarbamothioyl)carbamoyl)-[1,1'-biphenyl]-2-carboxylate (3ia)



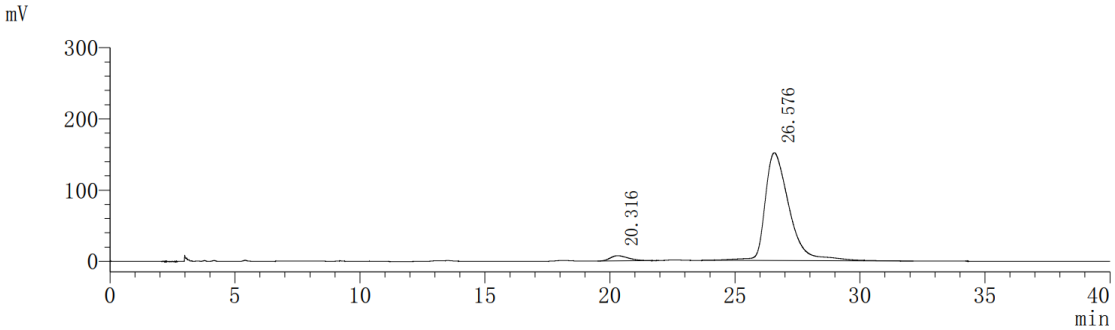
The title compound **3ia** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 2:1). **3ia** was obtained as a yellow oil (25.5 mg, 61%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.00 (s, 1H), 9.62 (s, 1H), 9.56 (d, *J* = 0.8 Hz, 1H), 8.15 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.11 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.94 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.59 (td, *J* = 7.7, 1.5 Hz, 3H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.27 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.21, 177.57, 168.60, 168.29, 142.65, 137.62, 135.66, 135.21, 134.13, 133.15, 132.88, 131.13, 131.04, 130.89, 129.95, 129.76, 128.96, 128.73, 126.86, 123.93, 53.30. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{23}H_{19}N_2O_4S$, ([M + H]$^+$), 419.1060; found 419.1051.

[α]$_D^{20}$ = -29.6 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 20.32 min, t_R (major) = 26.58 min, 93% ee.

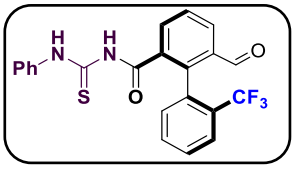


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.075	M	1.2343	6532051	130809	50.2963
2	25.943	M	1.4966	6455087	109983	49.7037



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.316	M	1.3084	373144	7320	3.5409
2	26.576	M	1.6881	10165059	151439	96.4591

(*R*)-6-formyl-*N*-(phenylcarbamothioyl)-2'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (3ja)

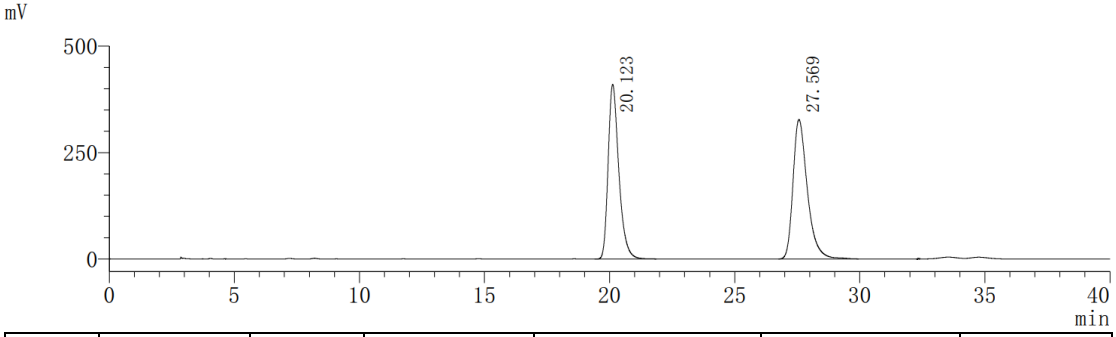


The title compound **3ja** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ja** was obtained as a yellow oil (26.9 mg, 63%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 11.98 (s, 1H), 9.59 (s, 1H), 8.63 (s, 1H), 8.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.05 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.68 – 7.65 (m, 1H), 7.59 – 7.57 (m, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.25 – 7.23 (m, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 189.82, 177.67, 166.80, 140.48, 137.53, 135.40, 134.25, 133.08, 132.97, 132.36, 131.95, 131.40, 129.92, 129.63, 129.31 (q, *J* = 29.9 Hz), 129.01, 127.13 (q, *J* = 5.2 Hz), 127.10, 124.13, 123.87 (q, *J* = 272.2 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -58.78 (s, 1CF_3).

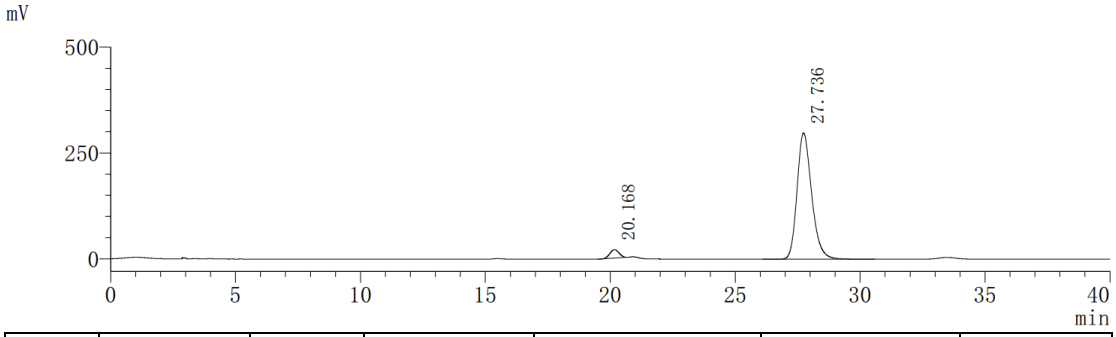
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{15}F_3N_2NaO_2S$, ($[M + Na]^+$), 451.0699; found 451.0699.

$[\alpha]_D^{20}$ = -28.0 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 20.17 min, t_R (major) = 27.74 min, 92% ee.

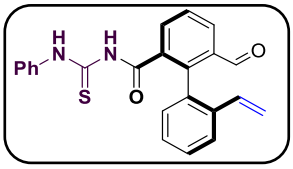


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.123	M	0.7591	12191329	410278	48.2337
2	27.569	M	1.0121	13084189	327854	51.7663



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.168	M	0.6938	504737	19853	3.9876
2	27.736	M	1.0564	12152974	298631	96.0124

(*R*)-6-formyl-*N*-(phenylcarbamothioyl)-2'-vinyl-[1,1'-biphenyl]-2-carboxamide (3ka)

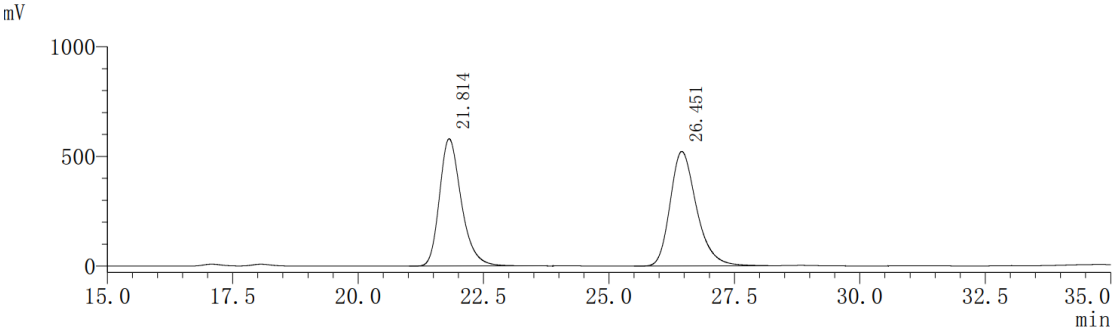


The title compound **3ka** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ka** was obtained as a yellow oil (27.0 mg, 70%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.08 (s, 1H), 9.65 (d, *J* = 0.8 Hz, 1H), 8.46 (s, 1H), 8.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.09 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.76 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.70 (td, *J* = 7.8, 0.8 Hz, 1H), 7.60 – 7.58 (m, 2H), 7.54 (td, *J* = 7.7, 1.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.3 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.28 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.38 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.75 (dd, *J* = 17.3, 0.8 Hz, 1H), 5.29 (dd, *J* = 11.0, 0.8 Hz, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.87, 177.61, 167.29, 142.37, 137.58, 137.48, 135.19, 134.59, 134.18, 133.65, 132.07, 131.26, 130.40, 130.26, 129.08, 128.99, 128.81, 127.01, 126.86, 124.08, 118.74.

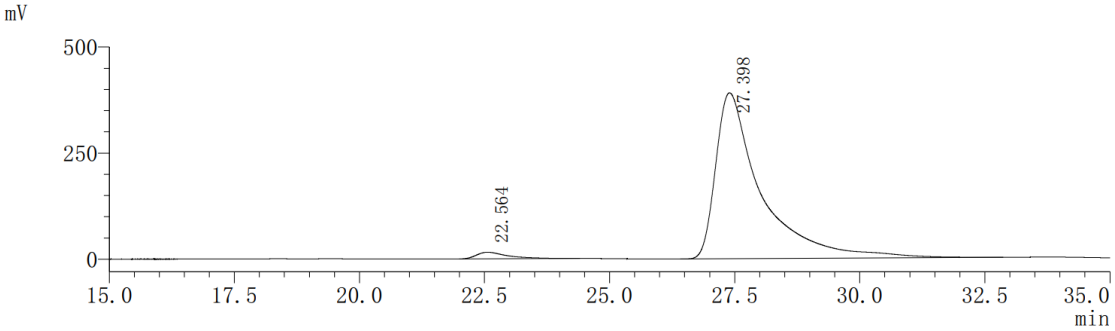
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{18}N_2NaO_2S$, ($[M + Na]^+$), 409.0981; found 409.0980.

$[\alpha]_D^{20}$ = -18.8 (c = 1.4, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 22.56 min, t_R (major) = 27.40 min, 95% ee.

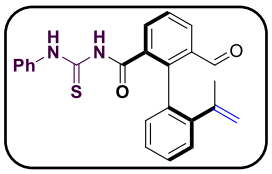


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	21.814	M	0.7757	17580171	580416	47.8992
2	26.451	M	0.9397	19122252	522116	52.1008



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	22.564	M	1.0735	669202	15660	2.6259
2	27.398	M	1.3463	24815579	391144	97.3741

(*R*)-6-formyl-*N*-(phenylcarbamothioyl)-2'-(prop-1-en-2-yl)-[1,1'-biphenyl]-2-carboxamide (3la)

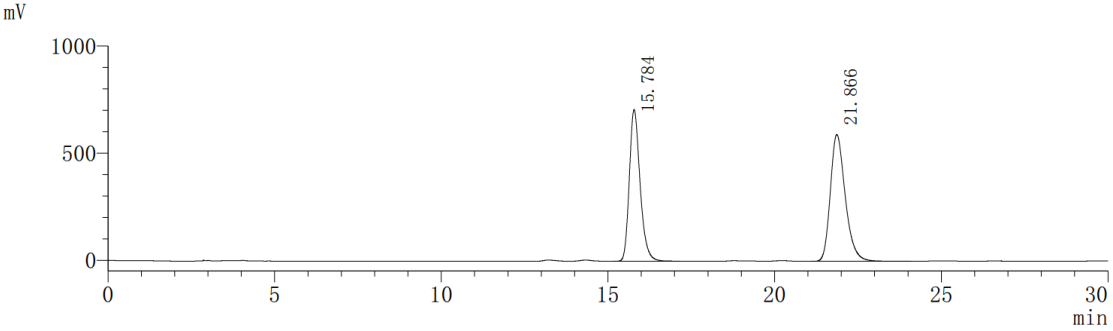


The title compound **3la** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3la** was obtained as a yellow oil (24.0 mg, 60%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 9.72 (d, *J* = 0.9 Hz, 1H), 8.47 (s, 1H), 8.22 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.08 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.67 (td, *J* = 7.8, 0.9 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.54 – 7.46 (m, 3H), 7.39 – 7.35 (m, 2H), 7.29 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 5.09 (p, *J* = 1.5 Hz, 1H), 4.88 (t, *J* = 1.3 Hz, 1H), 1.68 (t, *J* = 1.1 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.95, 177.77, 167.42, 144.22, 143.91, 143.61, 137.64, 135.14, 134.24, 133.91, 131.44, 131.14, 130.63, 130.41, 129.90, 129.02, 128.80, 128.38, 127.02, 124.11, 118.84, 23.20.

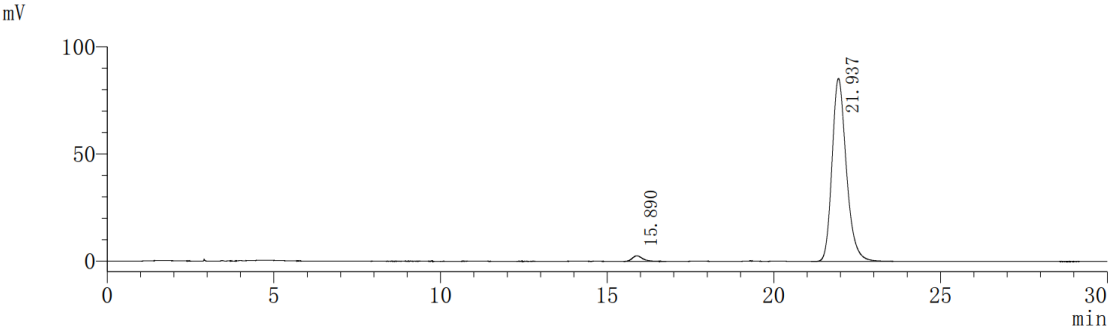
HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{20}N_2NaO_2S$, ($[M + Na]^+$), 423.1138; found 423.1131.

$[\alpha]_D^{20}$ = -36.0 (c = 1.2, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 15.89 min, t_R (major) = 21.94 min, 96% ee.

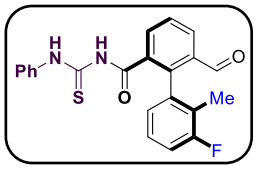


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.784	M	0.5762	15850315	707353	46.2565
2	21.866	M	0.8027	18415841	591568	53.7435

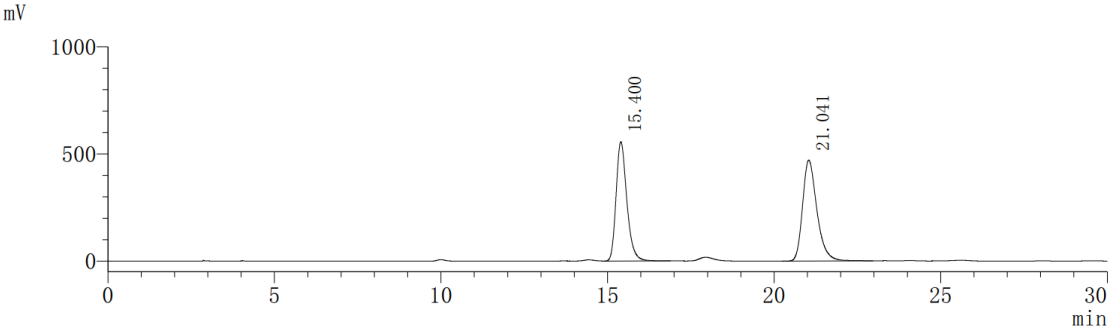


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.890	M	0.5594	55851	2589	2.1460
2	21.937	M	0.7725	2546664	85392	97.8540

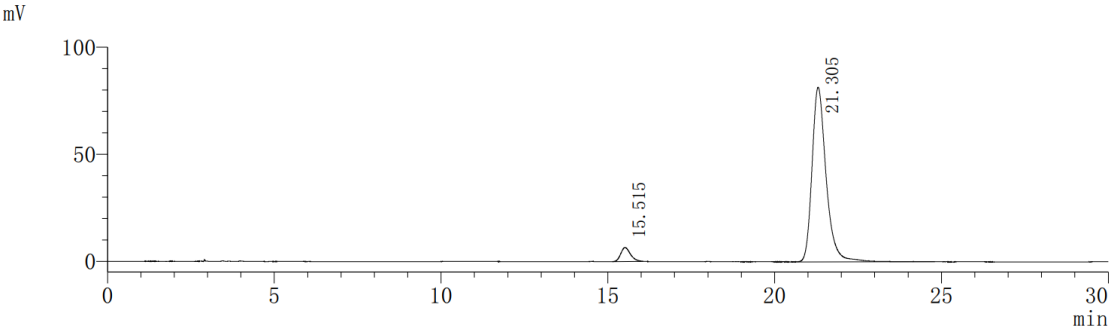
(*R*)-3'-fluoro-6-formyl-2'-methyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3ma)



The title compound **3ma** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ma** was obtained as a yellow oil (27.4 mg, 70%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.06 (s, 1H), 9.66 (d, *J* = 0.8 Hz, 1H), 8.57 (s, 1H), 8.24 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.09 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.72 (td, *J* = 7.7, 0.8 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.38 – 7.34 (m, 3H), 7.26 – 7.23 (m, 1H), 7.21 (td, *J* = 8.3, 1.1 Hz, 1H), 7.06 (dd, *J* = 7.5, 1.1 Hz, 1H), 2.06 (d, *J* = 2.2 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.51, 177.50, 167.00, 161.92 (d, *J* = 246.5 Hz), 141.86 (d, *J* = 2.7 Hz), 137.49, 135.76 (d, *J* = 4.4 Hz), 135.00, 134.23, 133.92, 131.39, 129.24, 129.03, 128.20 (d, *J* = 9.1 Hz), 127.10, 125.43 (d, *J* = 3.5 Hz), 124.71 (d, *J* = 17.3 Hz), 124.05, 116.76 (d, *J* = 22.5 Hz), 12.49 (d, *J* = 4.5 Hz). ^{19}F NMR (565 MHz, Chloroform-*d*) δ -113.48 – -113.50 (m, 1F).
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{17}FN_2NaO_2S$, ($[M + Na]^+$), 415.0887; found 415.0896.
$[\alpha]_D^{20}$ = -26.7 (c = 1.4, CH_2Cl_2).
HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 15.52 min, t_R (major) = 21.31 min, 90% ee.

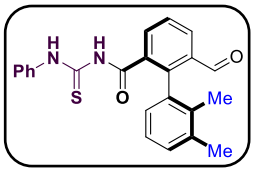


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.400	M	0.5759	12475223	556329	46.9402
2	21.041	M	0.7670	14101601	470739	53.0598



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.515	M	0.5247	131597	6532	5.1931
2	21.305	M	0.7449	2402486	81546	94.8069

(*R*)-6-formyl-2',3'-dimethyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3na)

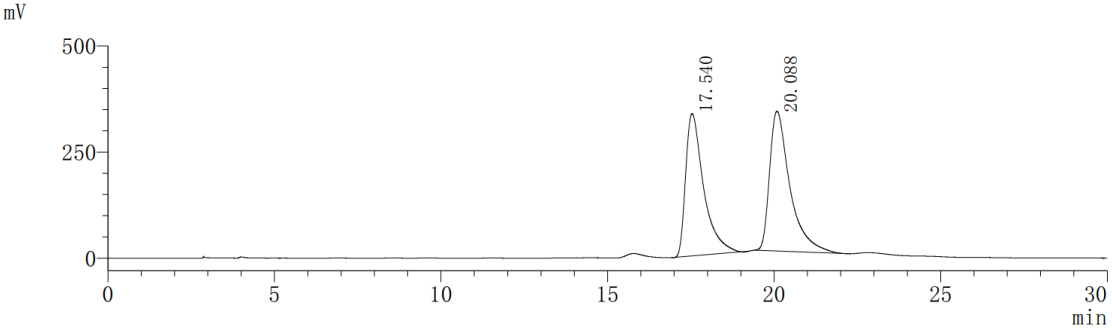


The title compound **3na** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3na** was obtained as a yellow oil (27.9 mg, 72%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 9.63 (d, *J* = 0.8 Hz, 1H), 8.50 (s, 1H), 8.22 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.18 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.37 – 7.33 (m, 3H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 2.39 (s, 3H), 2.07 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.18, 177.50, 167.03, 143.95, 139.17, 137.62, 135.04, 135.03, 134.77, 133.74, 133.24, 131.79, 131.26, 128.97, 128.74, 127.59, 126.93, 126.91, 123.97, 20.70, 17.16.

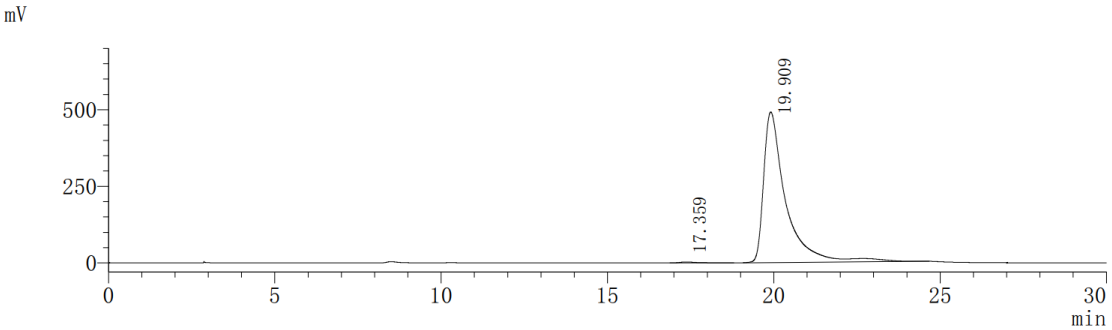
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{20}N_2NaO_2S$, ($[M + Na]^+$), 411.1138; found 411.1125.

$[\alpha]_D^{20}$ = -26.2 (c = 1.4, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 17.36 min, t_R (major) = 19.91 min, 99% ee.

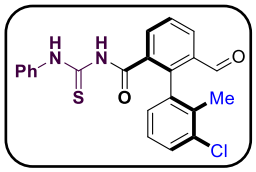


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	17.540	M	0.9257	12618520	335821	47.3899
2	20.088	M	1.0401	14008523	329812	52.6101



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	17.359	M	0.8973	135989	3481	0.5942
2	19.909	M	1.0109	22749575	490968	99.4058

(*R*)-3'-chloro-6-formyl-2'-methyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3oa)

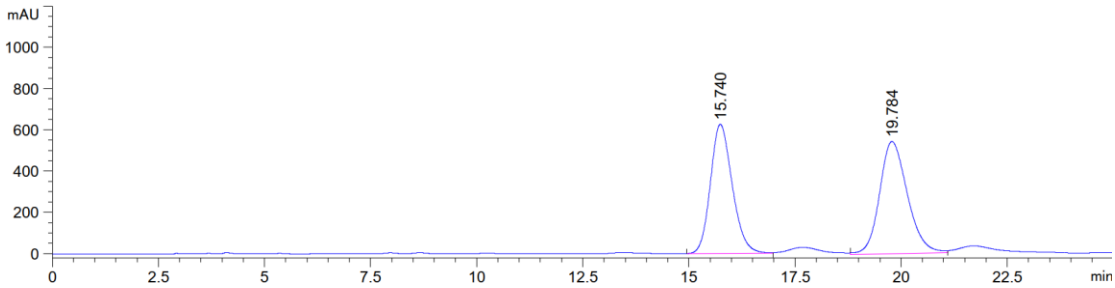


The title compound **3oa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3oa** was obtained as a yellow oil (27.3 mg, 67%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.02 (s, 1H), 9.65 (d, *J* = 0.9 Hz, 1H), 8.58 (s, 1H), 8.23 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.07 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.71 (td, *J* = 7.8, 0.9 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.54 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.39 – 7.36 (m, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.15 (dd, *J* = 7.7, 1.2 Hz, 1H), 2.18 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.45, 177.51, 166.96, 142.70, 137.50, 136.54, 135.44, 135.30, 134.99, 134.25, 133.70, 131.37, 130.83, 129.21, 129.02, 128.23, 127.61, 127.10, 124.07, 18.10.

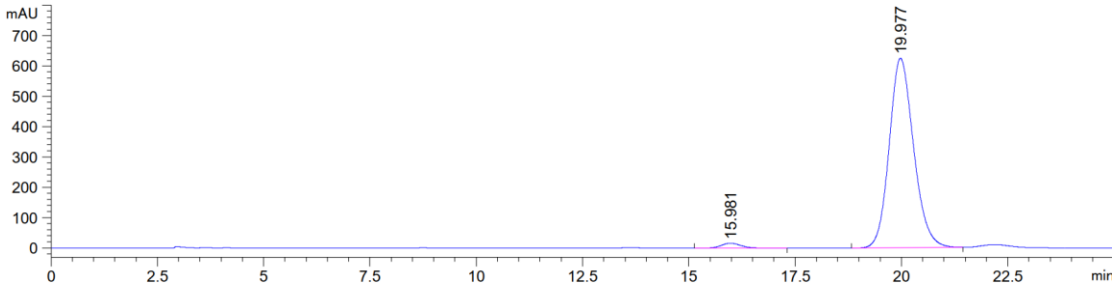
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{18}ClN_2O_2S$, ($[M + H]^+$), 409.0772; found 409.0763.

$[\alpha]_D^{20}$ = -32.4 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 15.98 min, t_R (major) = 19.98 min, 96% ee.

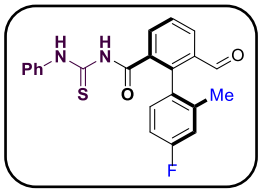


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	15.740	MM R	0.5970	2.24424e4	626.57648	47.5663
2	19.784	MM R	0.7586	2.47388e4	543.54486	52.4337



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	15.981	MM	0.4983	538.36951	16.51801	2.1169
2	19.977	MM	0.6162	2.48932e4	624.30591	97.8831

(*R*)-4'-fluoro-6-formyl-2'-methyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3pa)

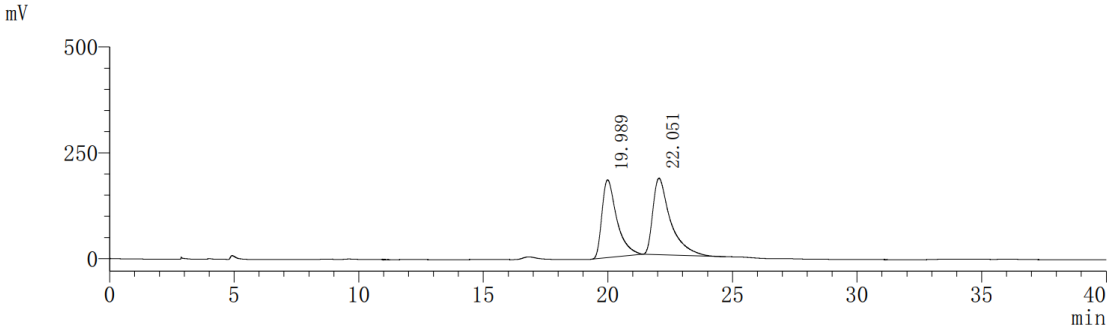


The title compound **3pa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3pa** was obtained as a yellow oil (27.4 mg, 70%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.08 (s, 1H), 9.65 (d, *J* = 0.8 Hz, 1H), 8.57 (s, 1H), 8.23 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.09 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.70 (td, *J* = 7.8, 0.9 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.13 (dd, *J* = 9.4, 2.6 Hz, 1H), 7.08 (td, *J* = 8.2, 2.7 Hz, 1H), 2.13 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.72, 177.53, 167.11, 163.40 (d, *J* = 248.1 Hz), 142.38, 139.52 (d, *J* = 8.2 Hz), 137.46, 135.20, 134.40, 133.94, 131.41, 131.33 (d, *J* = 8.6 Hz), 129.28 (d, *J* = 3.3 Hz), 129.11, 129.03, 127.10, 124.04, 118.11 (d, *J* = 21.5 Hz), 114.14 (d, *J* = 21.6 Hz), 20.62. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -111.45 – -111.50 (m, 1F).

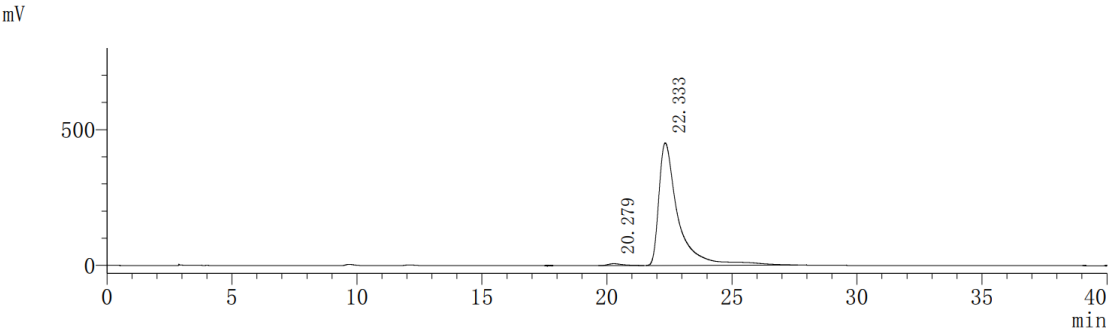
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{18}FN_2O_2S$, ($[M + H]^+$), 393.1068; found 393.1052.

$[\alpha]_D^{20}$ = -20.4 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 20.28 min, t_R (major) = 22.33 min, 97% ee.

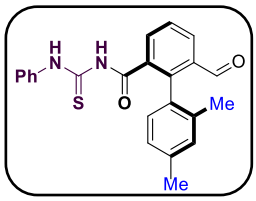


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	19.989	M	1.0480	7643918	183898	46.2648
2	22.051	M	1.1942	8878198	180498	53.7352



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.279	M	1.0758	330440	7366	1.3482
2	22.333	M	1.1871	24178834	451210	98.6518

(*R*)-6-formyl-2',4'-dimethyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3qa)

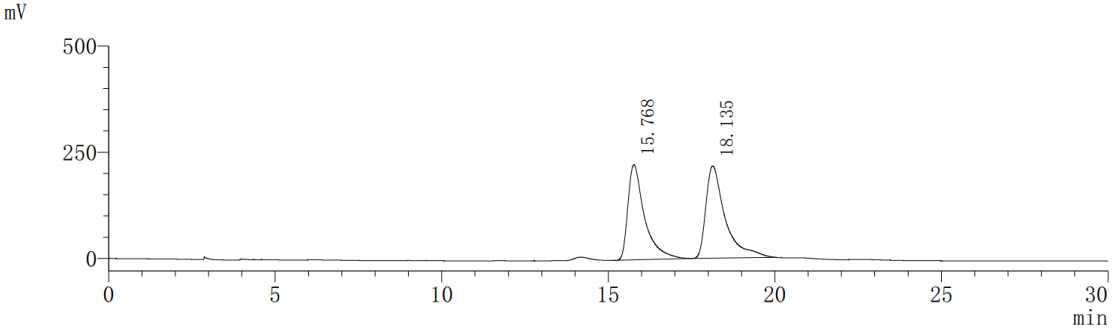


The title compound **3qa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3qa** was obtained as a yellow oil (33.0 mg, 85%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.20 (s, 1H), 9.65 (d, *J* = 0.9 Hz, 1H), 8.51 (s, 1H), 8.22 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.17 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.67 (td, *J* = 7.8, 0.9 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.38 – 7.35 (m, 2H), 7.25 – 7.20 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 1H), 2.41 (s, 3H), 2.09 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.22, 177.63, 167.16, 143.49, 140.34, 137.63, 136.33, 135.13, 134.69, 133.84, 132.27, 131.36, 130.06, 129.68, 128.97, 128.74, 128.01, 126.94, 124.02, 21.47, 20.28.

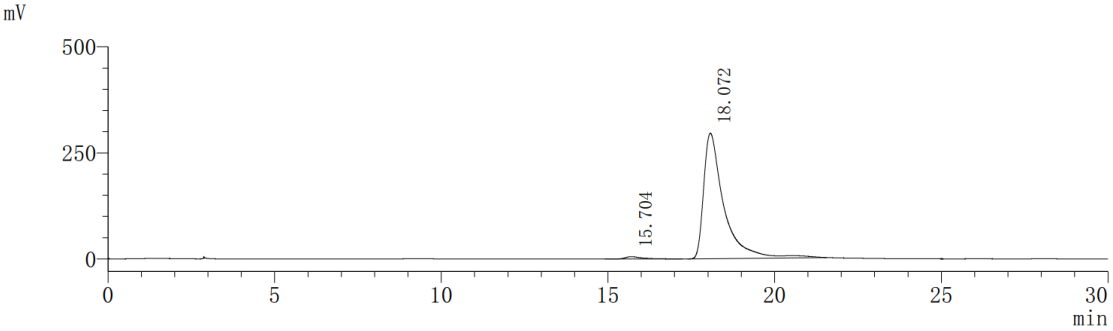
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{21}N_2O_2S$, ($[M + H]^+$), 389.1318; found 389.1311.

$[\alpha]_D^{20}$ = -25.2 (c = 1.6, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 15.70 min, t_R (major) = 18.07 min, 97% ee.

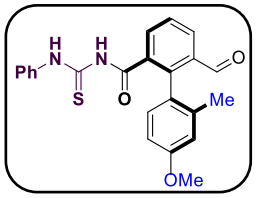


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.768	M	0.8241	7805998	224141	47.0985
2	18.135	M	0.9375	8767757	217332	52.9015



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.704	M	0.9044	215221	5648	1.6971
2	18.072	M	0.9508	12466214	295934	98.3029

(*R*)-6-formyl-4'-methoxy-2'-methyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3ra)

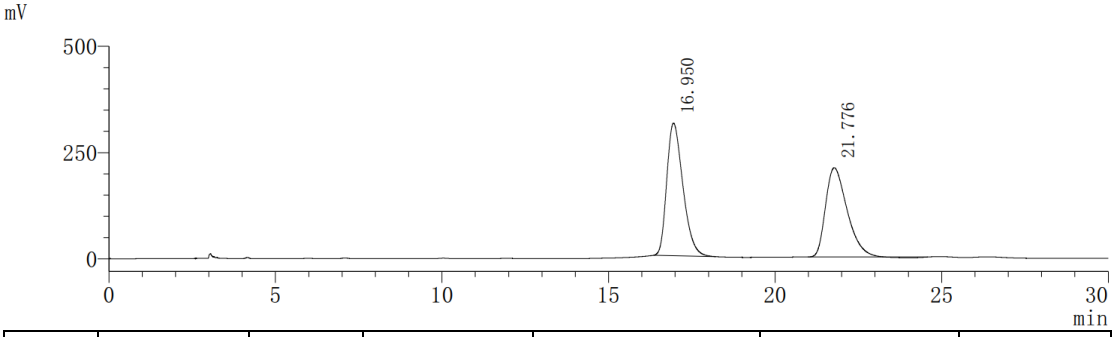


The title compound **3ra** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ra** was obtained as a yellow oil (32.7 mg, 81%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.20 (s, 1H), 9.67 (s, 1H), 8.54 (s, 1H), 8.21 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.16 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.67 (t, *J* = 7.8 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.38 – 7.35 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.96 – 6.92 (m, 2H), 3.87 (s, 3H), 2.11 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.29, 177.62, 167.20, 160.92, 143.17, 138.20, 137.64, 135.46, 134.65, 134.13, 131.37, 130.99, 128.98, 128.75, 126.95, 125.07, 124.00, 117.06, 112.84, 55.63, 20.67.

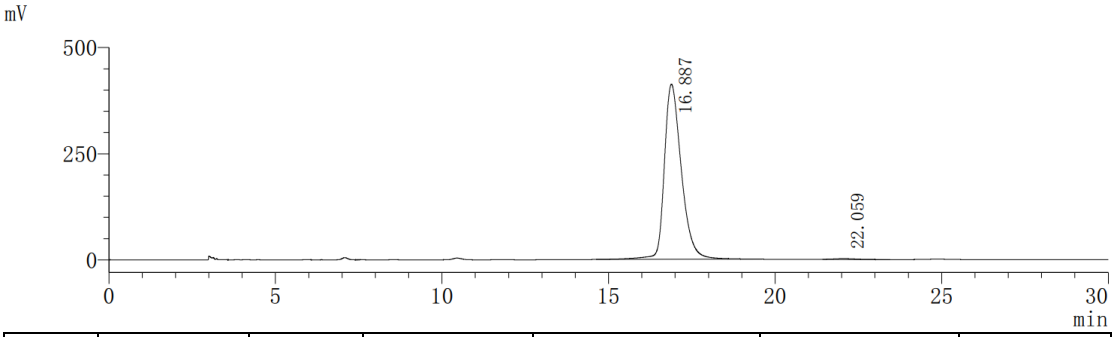
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{21}N_2O_3S$, ($[M + H]^+$), 405.1267; found 405.1261.

$[\alpha]_D^{20}$ = -32.0 (c = 1.6, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 16.89 min, t_R (minor) = 22.06 min, 99% ee.

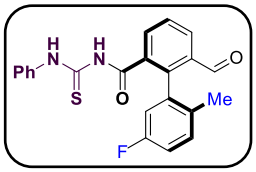


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	16.950	M	0.8894	10537414	312211	52.8848
2	21.776	M	1.1930	9387812	210108	47.1152



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	16.887	M	0.9010	14691922	412657	99.4744
2	22.059	M	1.0797	77634	1892	0.5256

(*R*)-5'-fluoro-6-formyl-2'-methyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3sa)

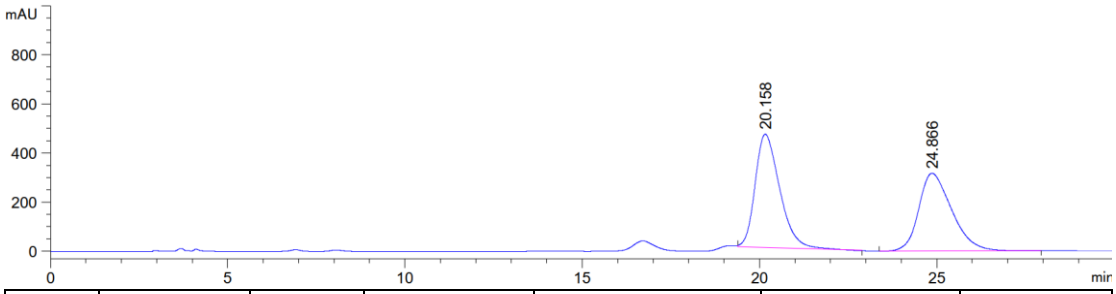


The title compound **3sa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3sa** was obtained as a yellow oil (29.4 mg, 75%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.07 (s, 1H), 9.65 (s, 1H), 8.64 (s, 1H), 8.23 (dd, *J* = 7.9, 1.5 Hz, 1H), 8.10 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 1H), 7.62 – 7.60 (m, 2H), 7.39 – 7.35 (m, 3H), 7.26 – 7.23 (m, 1H), 7.14 (td, *J* = 8.4, 2.8 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.8 Hz, 1H), 2.10 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.49, 177.57, 166.90, 161.32 (d, *J* = 246.4 Hz), 142.12, 137.51, 135.05 (d, *J* = 7.3 Hz), 134.83, 134.02, 133.97, 132.76 (d, *J* = 8.1 Hz), 132.49 (d, *J* = 3.4 Hz), 131.43, 129.26, 129.02, 127.09, 124.08, 116.97 (d, *J* = 20.5 Hz), 116.71 (d, *J* = 22.1 Hz), 19.61. **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -115.41 – -115.45 (m, 1F).

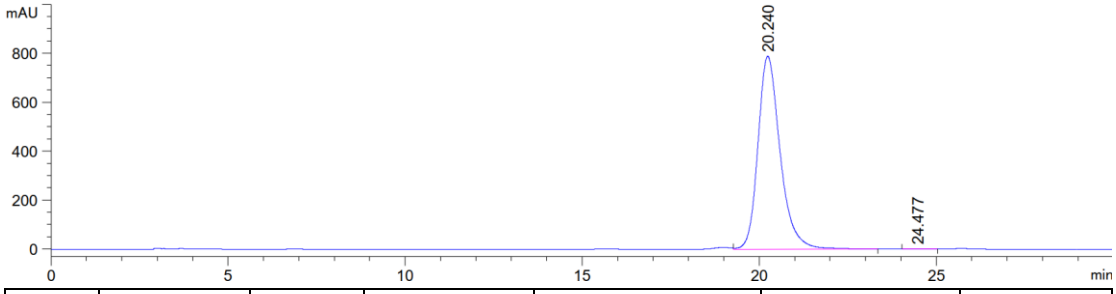
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{18}FN_2O_2S$, ($[M + H]^+$), 393.1068; found 393.1062.

$[\alpha]_D^{20}$ = -35.6 (c = 1.5, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 20.24 min, t_R (minor) = 24.48 min, 99% ee.

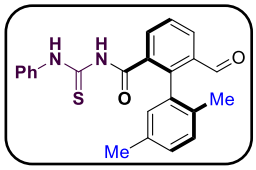


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	20.158	MM	0.8023	2.21882e4	460.91681	52.0782
2	24.866	MM	1.0098	2.04174e4	316.40860	47.9218



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	20.240	MM	0.7259	3.43356e4	788.31769	99.8955
2	24.477	MM	0.5497	35.91503	1.08898	0.1045

(*R*)-6-formyl-2',5'-dimethyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3ta)

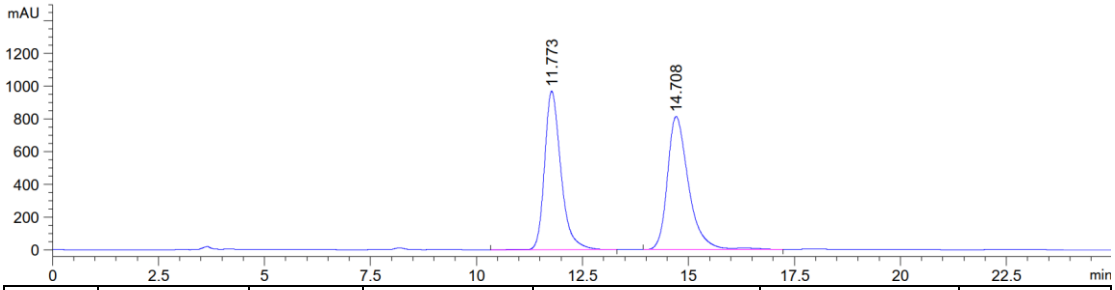


The title compound **3ta** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ta** was obtained as a yellow oil (27.9 mg, 72%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.19 (s, 1H), 9.64 (s, 1H), 8.56 (s, 1H), 8.23 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.63 – 7.61 (m, 2H), 7.38 – 7.35 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.09 (d, *J* = 1.8 Hz, 1H), 2.40 (s, 3H), 2.07 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.14, 177.51, 167.05, 143.44, 137.66, 137.16, 134.94, 134.73, 133.69, 133.42, 133.03, 131.46, 131.29, 131.10, 130.18, 128.95, 128.77, 126.89, 123.94, 21.14, 19.80.

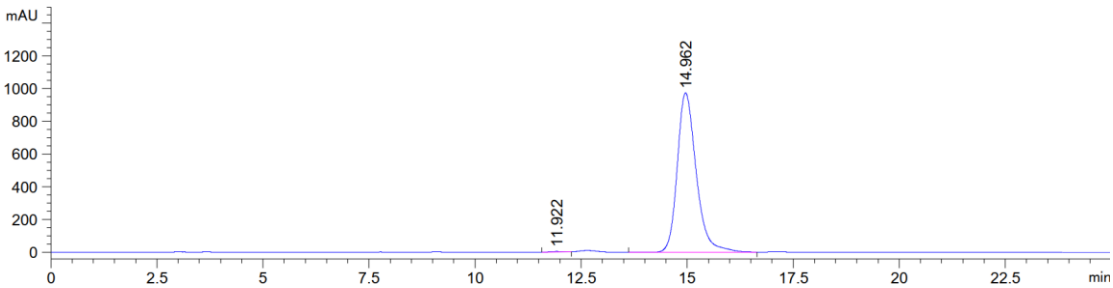
HRMS (ESI-TOF) (m/z): Calcd for $C_{23}H_{21}N_2O_2S$, ($[M + H]^+$), 389.1318; found 389.1308.

$[\alpha]_D^{20}$ = -6.3 (c = 1.4, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 11.92 min, t_R (major) = 14.96 min, 99% ee.

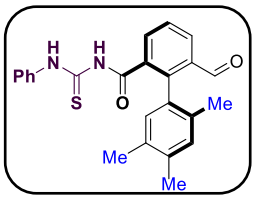


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	11.773	MM	0.4072	2.59456e4	969.48193	47.8652
2	14.708	MM	0.5217	2.82599e4	813.44824	52.1348



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	11.922	MM	0.3696	91.64922	4.13329	0.3023
2	14.962	MM	0.4731	3.02290e4	973.98560	99.6977

(*R*)-6-formyl-2',4',5'-trimethyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3ua)

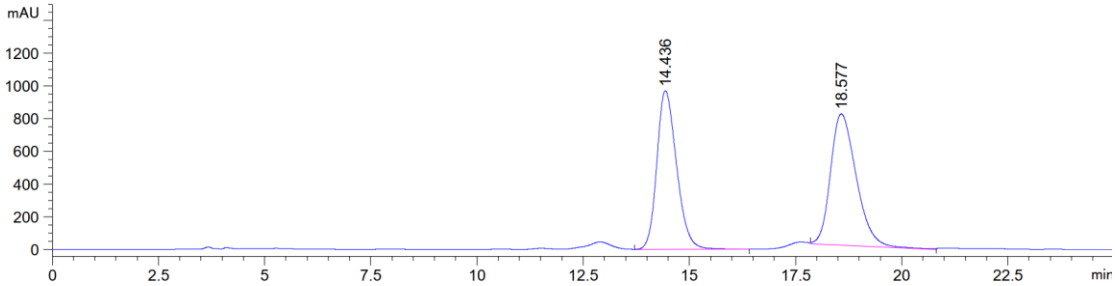


The title compound **3ua** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ua** was obtained as a yellow oil (33.4 mg, 83%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.24 (s, 1H), 9.68 (s, 1H), 8.21 (td, *J* = 8.2, 1.5 Hz, 2H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.38 – 7.35 (m, 2H), 7.25 – 7.21 (m, 1H), 7.19 (s, 1H), 7.03 (s, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.04 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.19, 177.44, 166.87, 143.42, 138.93, 137.56, 135.80, 134.92, 134.86, 133.49, 133.45, 132.73, 131.18, 130.49, 130.06, 128.79, 128.48, 126.69, 123.77, 19.58, 19.51, 19.33.

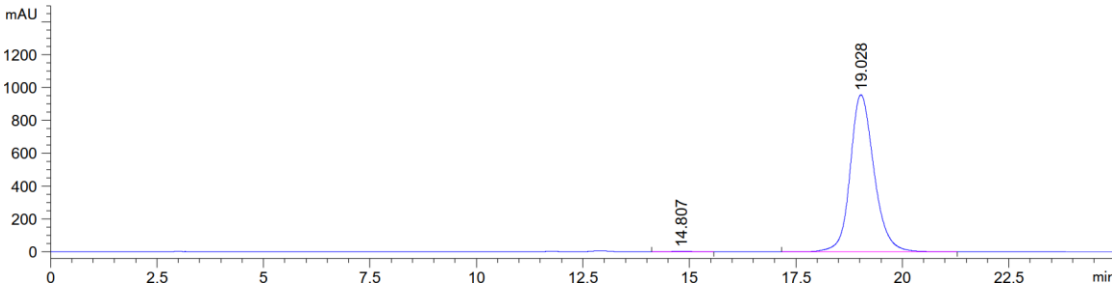
HRMS (ESI-TOF) (m/z): Calcd for $C_{24}H_{23}N_2O_2S$, ($[M + H]^+$), 403.1475; found 403.1465.

$[\alpha]_D^{20}$ = -6.2 (c = 1.6, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 14.81 min, t_R (minor) = 19.03 min, 99% ee.

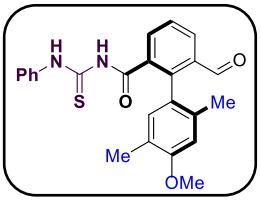


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.436	MM	0.4975	3.13043e4	969.98309	48.0089
2	18.577	MM	0.7035	3.39009e4	803.19098	51.9911



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.807	MM	0.4506	133.58797	4.51015	0.3571
2	19.028	MM	0.5964	3.72798e4	957.10712	99.6429

(*R*)-4'-ethoxy-6-formyl-2',5'-dimethyl-*N*-(phenylcarbamothioyl)-[1,1'-biphenyl]-2-carboxamide (3va)

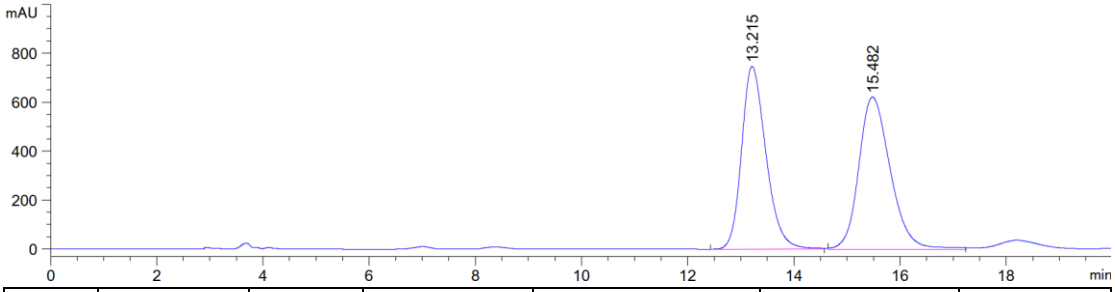


The title compound **3va** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3va** was obtained as a yellow oil (32.0 mg, 74%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.27 (s, 1H), 9.68 (s, 1H), 8.58 (s, 1H), 8.23 – 8.20 (m, 2H), 7.67 – 7.63 (m, 3H), 7.38 – 7.35 (m, 2H), 7.25 – 7.21 (m, 1H), 7.01 (s, 1H), 6.84 (s, 1H), 4.10 (q, *J* = 7.0 Hz, 2H), 2.24 (s, 3H), 2.08 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.51, 177.62, 167.06, 158.57, 143.54, 137.77, 135.45, 135.10, 135.07, 133.74, 131.68, 131.36, 128.95, 128.57, 126.83, 126.55, 123.98, 123.92, 114.09, 64.03, 20.35, 16.04, 15.08.

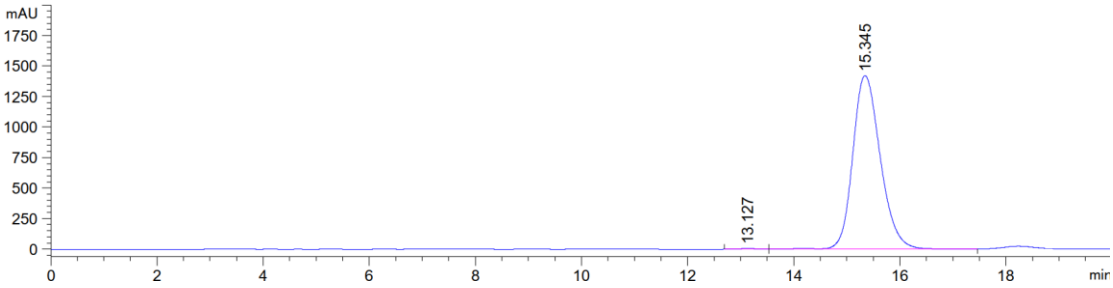
HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{25}N_2NaO_3S$, ($[M + H]^+$), 433.1580; found 433.1577.

$[\alpha]_D^{20}$ = -25.8 (c = 1.6, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 13.13 min, t_R (major) = 15.35 min, 99% ee.

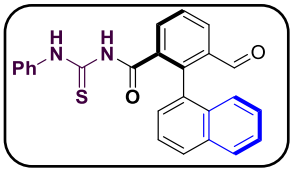


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	13.215	MM	0.4890	2.38458e4	745.89032	48.1684
2	15.482	MM	0.6877	2.56593e4	621.87701	51.8316



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	13.127	MM	0.3574	86.04757	3.81119	0.1683
2	15.345	MM	0.5556	5.10477e4	1420.08655	99.8317

(*R*)-3-formyl-2-(naphthalen-1-yl)-*N*-(phenylcarbamothioyl)benzamide (3wa)

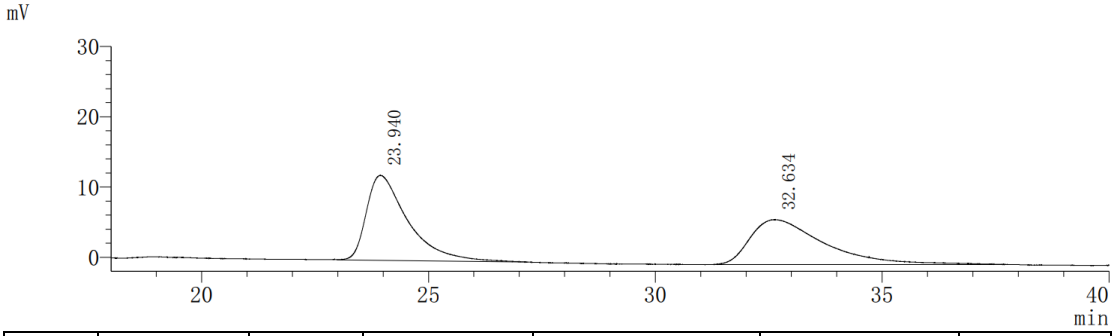


The title compound **3wa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3wa** was obtained as a yellow oil (25.8 mg, 63%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.88 (s, 1H), 9.49 (d, *J* = 0.9 Hz, 1H), 8.40 (s, 1H), 8.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.16 (dd, *J* = 7.7, 1.5 Hz, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.78 (td, *J* = 7.8, 0.9 Hz, 1H), 7.65 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.53 – 7.50 (m, 2H), 7.47 – 7.45 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.20 – 7.17 (m, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.88, 177.29, 167.25, 141.93, 137.45, 135.92, 135.22, 134.24, 133.93, 132.62, 131.22, 131.17, 130.54, 129.25, 129.23, 128.90, 128.57, 128.16, 127.18, 126.92, 125.63, 124.91, 123.99.

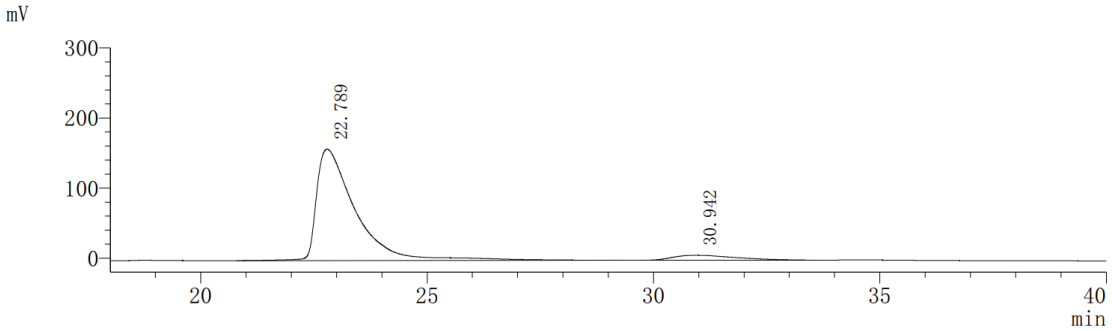
HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{19}N_2NaO_2S$, ($[M + H]^+$), 411.1162; found 411.1166.

$[\alpha]_D^{20}$ = -35.8 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 22.79 min, t_R (minor) = 30.94 min, 87% ee.

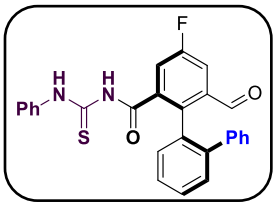


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	23.940	M	1.5878	768796	12086	51.3949
2	32.634	M	3.0195	727064	6402	48.6051



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	22.789	M	1.4288	9515843	158969	93.3491
2	30.942	M	2.4342	677982	6984	6.6509

(*R*)-4-fluoro-6-formyl-*N*-(phenylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3xa)

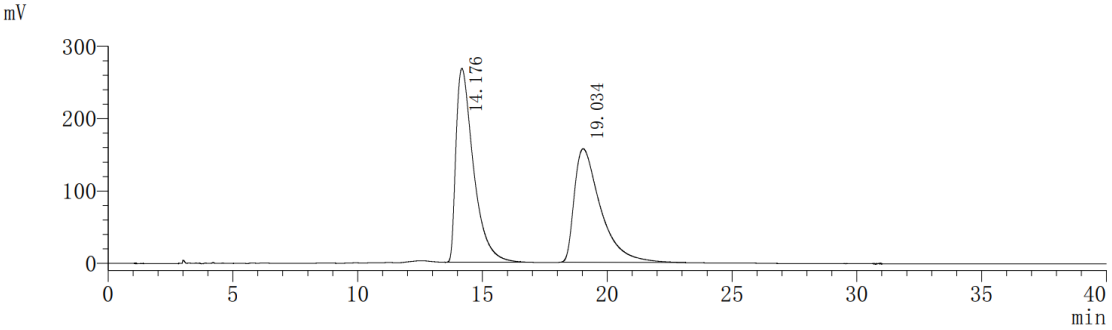


The title compound **3xa** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3xa** was obtained as a yellow oil (19.5 mg, 43%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.96 (s, 1H), 9.81 (d, *J* = 3.0 Hz, 1H), 8.26 (s, 1H), 7.81 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.66 – 7.56 (m, 6H), 7.41 – 7.38(m, 3H), 7.29 – 7.20 (m, 4H), 7.06 – 7.04 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 189.68, 177.45, 165.63 (d, *J* = 2.0 Hz), 161.88 (d, *J* = 251.2 Hz), 142.32, 139.63 (d, *J* = 3.8 Hz), 139.28, 137.59 (d, *J* = 6.2 Hz), 137.55, 136.18 (d, *J* = 6.0 Hz), 131.55, 131.43, 131.27, 130.77, 129.54, 129.09, 128.74, 128.55, 127.93, 127.14, 124.07, 121.10 (d, *J* = 23.8 Hz), 117.91 (d, *J* = 21.8 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -110.22 – -110.25 (m, 1F).

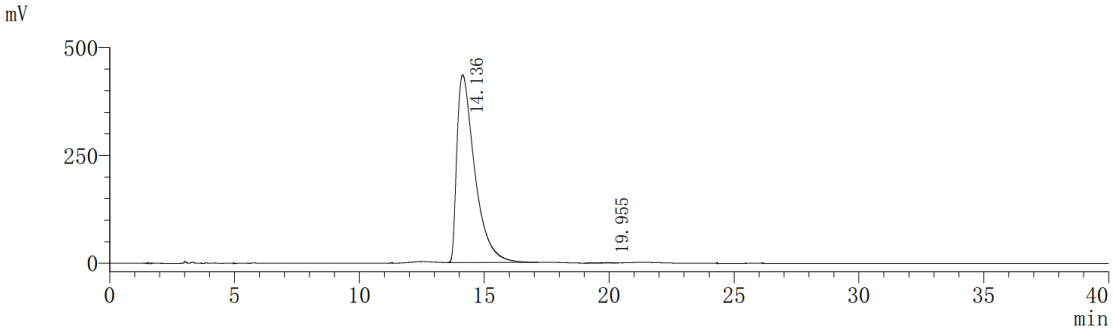
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{19}FN_2NaO_2S$, ($[M + Na]^+$), 477.1043; found 477.1050.

$[\alpha]_D^{20}$ = -138.9 (c = 1.0, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 14.14 min, t_R (minor) = 19.96 min, 99% ee.

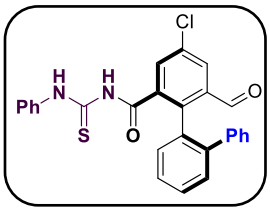


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.176	M	1.2359	13096587	267900	53.1803
2	19.034	M	1.8606	11530162	157003	46.8197



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.136	M	1.2576	21600411	435060	99.9247
2	19.955	M	1.2000	16275	355	0.0753

(*R*)-4-chloro-6-formyl-*N*-(phenylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ya)

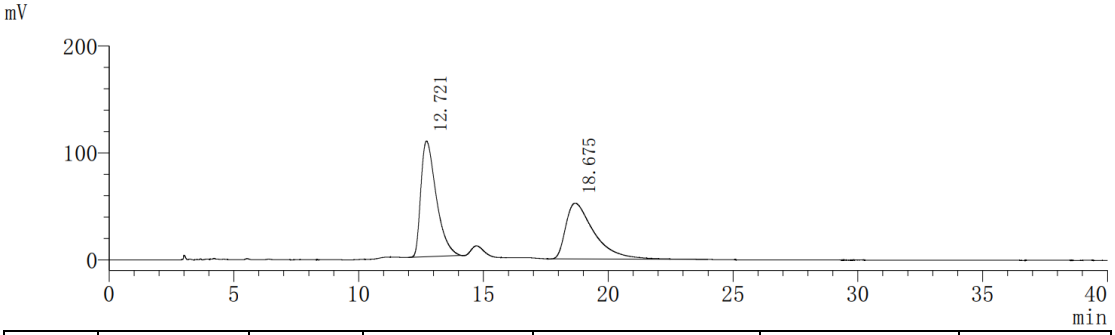


The title compound **3ya** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ya** was obtained as a yellow oil (21.6 mg, 46%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.94 (s, 1H), 9.81 (s, 1H), 8.26 (s, 1H), 8.08 (d, *J* = 2.4 Hz, 1H), 7.80 (d, *J* = 2.4 Hz, 1H), 7.65 – 7.55 (m, 5H), 7.41 – 7.35 (m, 3H), 7.29 – 7.21 (m, 4H), 7.07 – 7.05j (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 189.63, 177.49, 165.78, 142.13, 141.93, 139.22, 137.53, 136.77, 135.81, 135.18, 133.29, 131.40, 131.37, 131.22, 131.20, 130.76, 129.55, 129.10, 128.80, 128.49, 128.00, 127.16, 124.10.

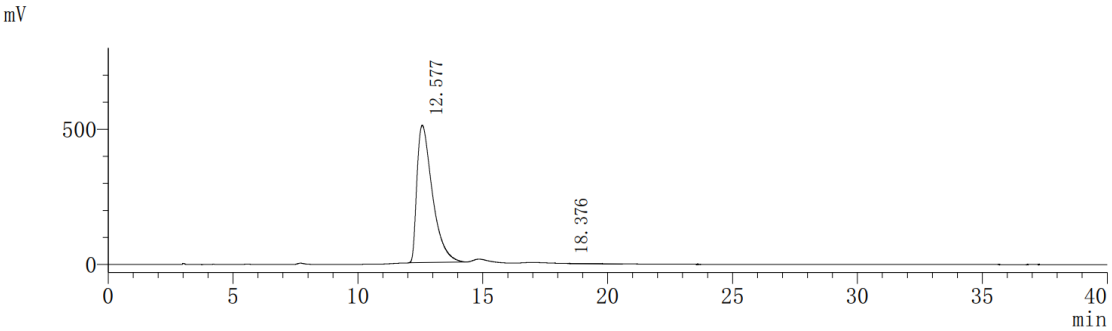
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{19}ClN_2NaO_2S$, ($[M + Na]^+$), 493.0748; found 493.0751.

$[\alpha]_D^{20}$ = -121.9 (c = 1.2, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 12.58 min, t_R (minor) = 18.38 min, 99% ee.

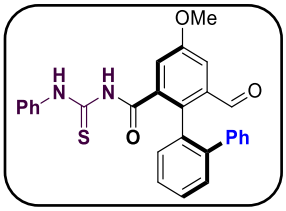


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	12.721	M	1.1223	4661971	108242	52.9519
2	18.675	M	2.0148	4142197	52255	47.0481



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	12.577	M	1.1100	21883409	507776	99.5263
2	18.376	M	3.9558	104161	631	0.4737

(*R*)-6-formyl-4-methoxy-*N*-(phenylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3za)

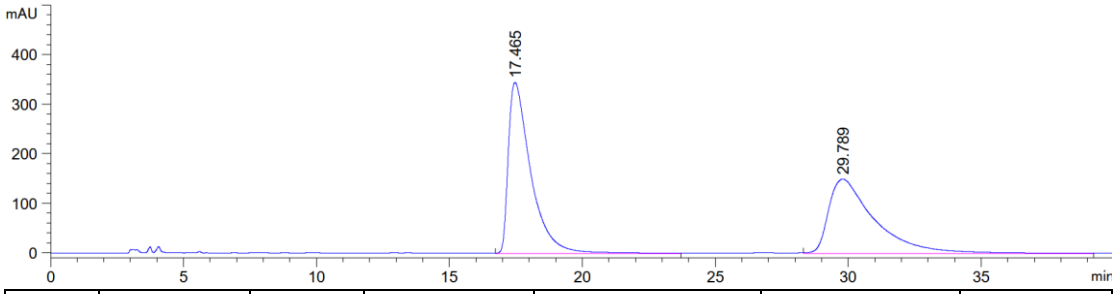


The title compound **3za** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3za** was obtained as a yellow oil (30.8 mg, 66%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.03 (s, 1H), 9.83 (s, 1H), 8.28 (s, 1H), 7.63 – 7.52 (m, 6H), 7.41 – 7.35 (m, 4H), 7.28 – 7.20 (m, 4H), 7.08 – 7.06 (m, 2H), 3.90 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.97, 177.75, 166.90, 159.21, 142.33, 139.68, 137.65, 136.74, 136.17, 135.46, 132.07, 131.90, 131.16, 130.20, 129.58, 129.04, 128.62, 128.25, 127.70, 127.02, 124.09, 120.64, 114.54, 56.07..

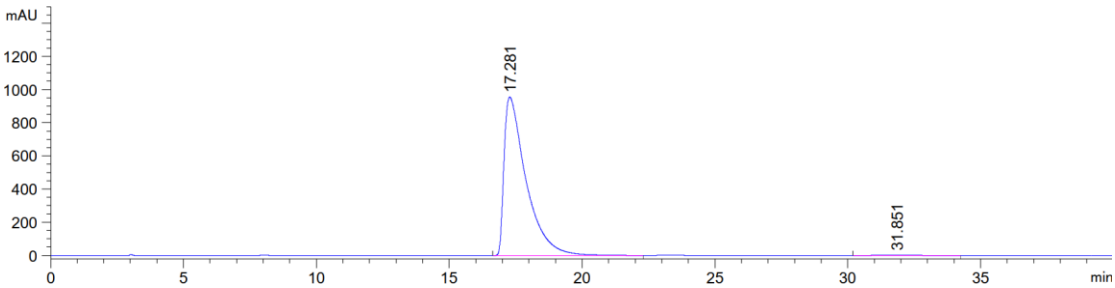
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}N_2NaO_3S$, ($[M + Na]^+$), 489.1243; found 489.1244.

$[\alpha]_D^{20}$ = -87.7 (c = 1.5, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 17.28 min, t_R (minor) = 31.85 min, 99% ee.

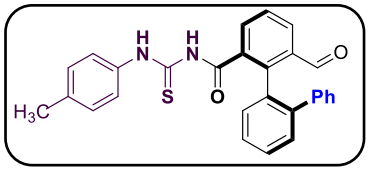


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	17.465	MM R	0.9873	2.04694e4	345.56125	52.7558
2	29.789	MM R	2.0340	1.83309e4	150.20439	47.2442



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	17.281	BB	0.8597	5.50036e4	955.27869	99.3899
2	31.851	BB	1.4116	337.64969	2.89088	0.6101

(*R*)-6-formyl-*N*-(p-tolylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ab)

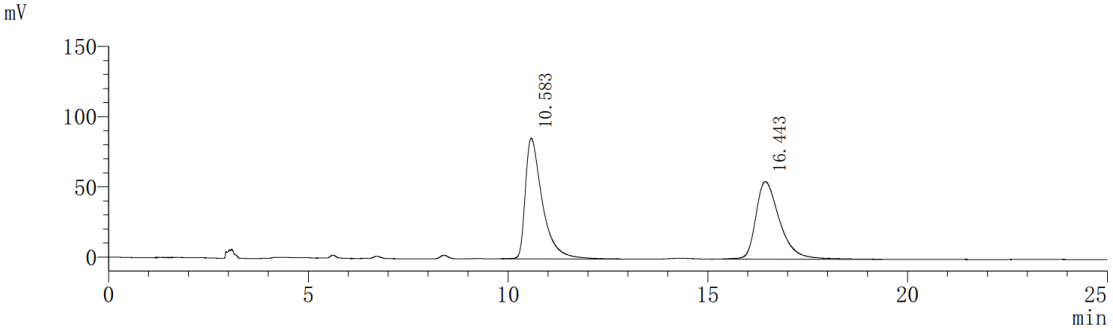


The title compound **3ab** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ab** was obtained as a yellow oil (19.8 mg, 44%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.93 (s, 1H), 9.87 (s, 1H), 8.22 (s, 1H), 8.13 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.81 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.59 – 7.54 (m, 3H), 7.49 – 7.47 (m, 2H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.18 (m, 5H), 7.08 – 7.06 (m, 2H), 2.36 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.04, 177.92, 167.22, 143.96, 142.02, 139.53, 137.06, 135.58, 135.08, 134.39, 133.26, 132.33, 131.45, 131.43, 131.14, 130.37, 129.65, 129.59, 128.62, 128.50, 128.27, 127.81, 124.21, 21.29.

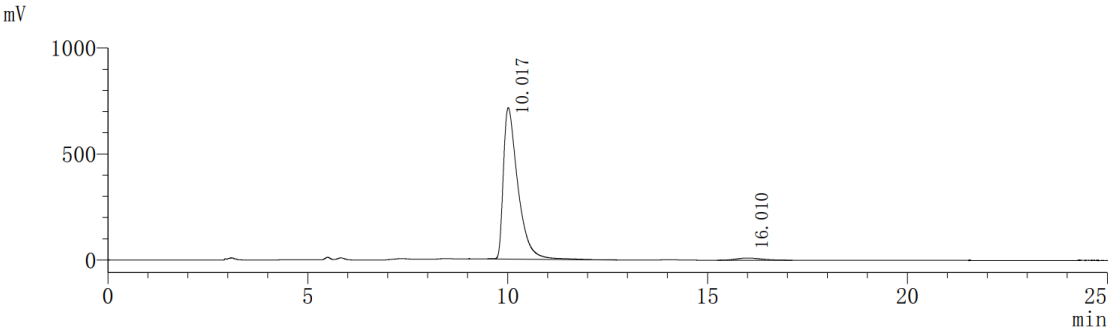
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{23}N_2O_2S$, ([M + Na]$^+$), 451.1475; found 451.1479.

[α]$_D^{20}$ = -30.0 (c = 1.0, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 10.02 min, t_R (minor) = 16.01 min, 95% ee.

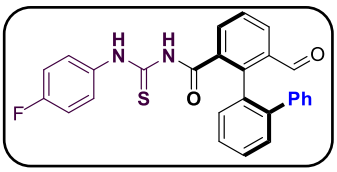


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.583	M	0.7406	2554940	85925	52.5428
2	16.443	M	1.0529	2307644	55304	47.4572

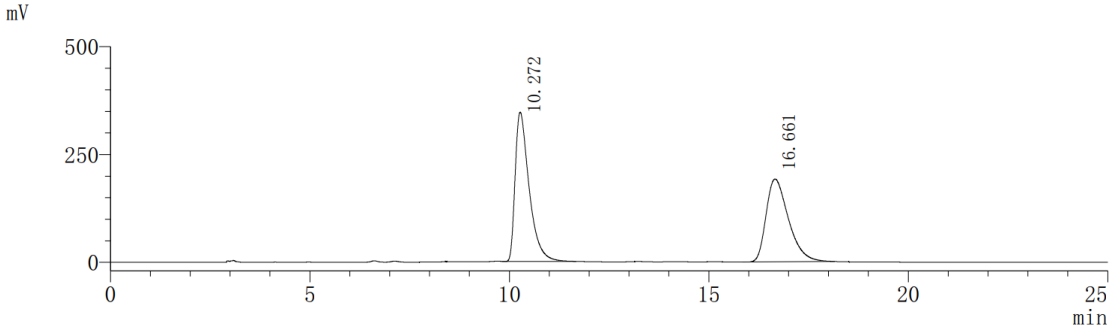


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.017	M	0.6340	18008463	713853	97.4931
2	16.010	M	1.1254	463066	10718	2.5069

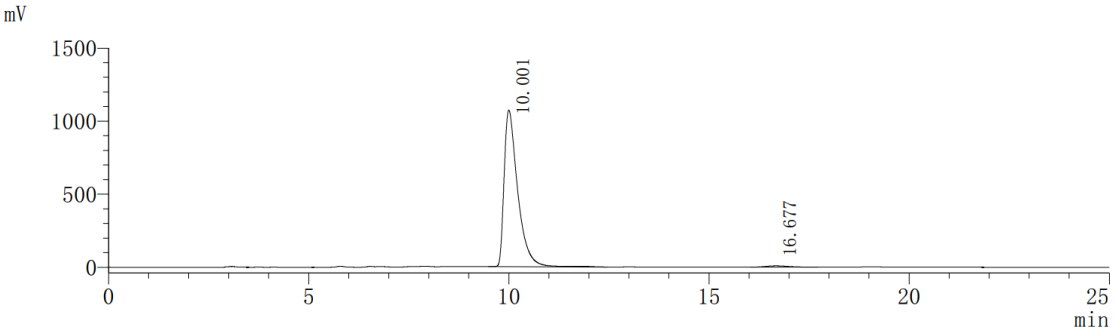
(*R*)-*N*-((4-fluorophenyl)carbamothioyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ac)



The title compound **3ac** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ac** was obtained as a yellow oil (20.4 mg, 45%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.97 (s, 1H), 9.87 (s, 1H), 8.26 (s, 1H), 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.59 – 7.55 (m, 5H), 7.39 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.10 – 7.05 (m, 4H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.96, 178.36, 167.33, 161.13 (d, *J* = 245.5 Hz), 143.93, 142.01, 139.50, 135.60, 134.19, 133.62 (d, *J* = 3.1 Hz), 133.31, 132.29, 131.57, 131.41, 131.17, 130.42, 129.56, 128.62, 128.5, 128.30, 127.83, 126.24 (d, *J* = 8.2 Hz), 115.94 (d, *J* = 22.8 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -114.19 – -114.23 (m, 1F).
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{19}FN_2NaO_2S$, ($[M + Na]^+$), 477.1043; found 477.1088.
$[\alpha]_D^{20}$ = -32.7 (c = 1.0, CH_2Cl_2).
HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 10.00 min, t_R (minor) = 16.68 min, 97% ee.

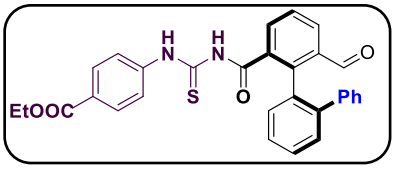


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.272	M	0.6170	8418989	346269	52.8922
2	16.661	M	1.0203	7498271	192188	47.1078



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	10.001	M	0.5926	25322382	1070888	98.5111
2	16.677	M	1.0781	382731	9367	1.4889

ethyl (*R*)-4-(3-(6-formyl-[1,1':2',1''-terphenyl]-2-carbonyl)thioureido)benzoate (3ad)

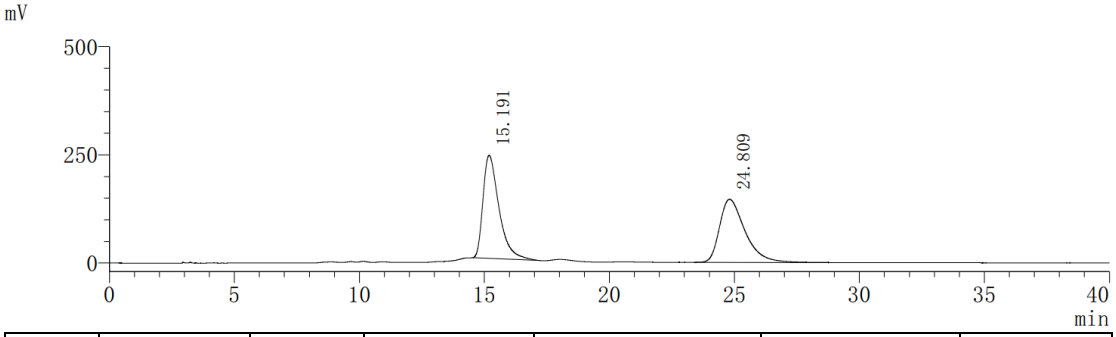


The title compound **3ad** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 2:1). **3ad** was obtained as a yellow oil (33.5 mg, 66%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.30 (s, 1H), 9.86 (s, 1H), 8.31 (s, 1H), 8.14 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.07 – 8.06 (m, 2H), 7.84 – 7.79 (m, 3H), 7.64 – 7.61 (m, 1H), 7.59 – 7.54 (m, 3H), 7.39 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.06 – 7.04 (m, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.88, 177.45, 167.32, 165.93, 143.83, 142.02, 141.55, 139.44, 135.59, 134.06, 133.43, 132.19, 131.62, 131.38, 131.22, 130.53, 130.51, 130.46, 129.54, 128.60, 128.54, 128.34, 127.83, 122.96, 61.23, 14.49.

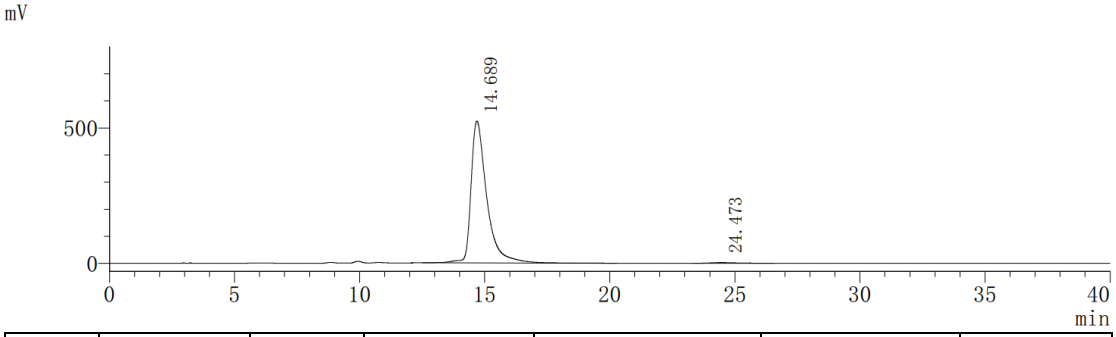
HRMS (ESI-TOF) (m/z): Calcd for $C_{30}H_{24}N_2NaO_4S$, ($[M + Na]^+$), 531.1349; found 531.1389.

$[\alpha]_D^{20}$ = -107.6 (c = 1.7, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 14.69 min, t_R (minor) = 24.47 min, 98% ee.

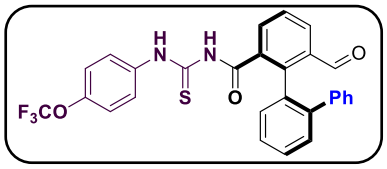


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.191	M	1.1456	10600168	238147	50.6636
2	24.809	M	1.8173	10322503	145809	49.3364



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.689	M	1.0575	22965154	523791	99.1622
2	24.473	M	1.7893	194035	2628	0.8378

(*R*)-6-formyl-*N*-((4-(trifluoromethoxy)phenyl)carbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ae)

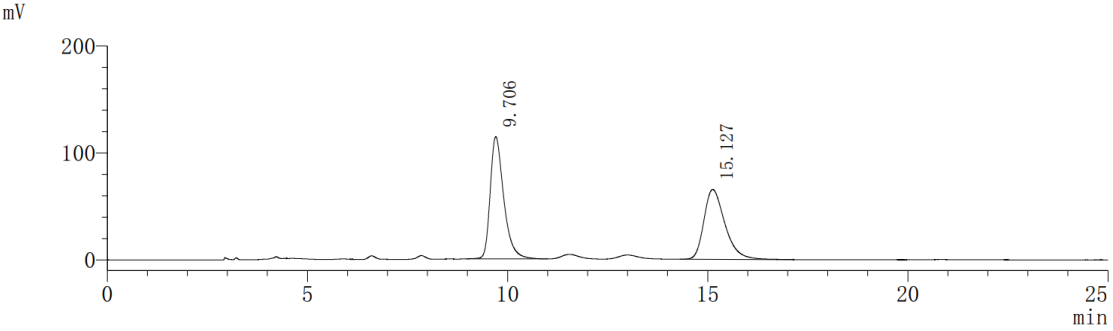


The title compound **3ae** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 2:1). **3ae** was obtained as a white solid (32.2 mg, 62%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.12 (s, 1H), 9.87 (s, 1H), 8.29 (s, 1H), 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.71 – 7.69 (m, 2H), 7.63 (td, *J* = 7.5, 1.4 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.39 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.26 – 7.18 (m, 5H), 7.06 – 7.05 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.90, 177.99, 167.36, 147.32, 143.86, 142.02, 139.47, 136.15, 135.62, 134.09, 133.39, 132.23, 131.63, 131.40, 131.21, 130.46, 129.54, 128.61, 128.55, 128.33, 127.84, 125.36, 121.53, 120.59 (q, *J* = 255.9 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -57.95 (s, 1CF_3).

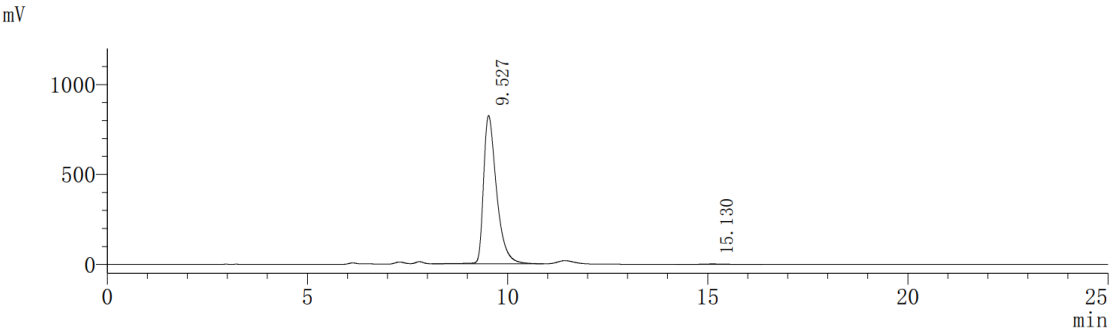
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{19}F_3N_2NaO_3S$, ($[M + Na]^+$), 543.0961; found 543.0944.

$[\alpha]_D^{20}$ = -108.1 (c = 1.6, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 9.53 min, t_R (minor) = 15.13 min, 99% ee.

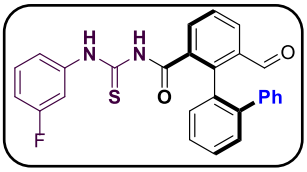


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	9.706	M	0.5964	2695880	114280	53.0997
2	15.127	M	0.9431	2381139	65262	46.9003



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	9.527	M	0.5715	18644442	824229	99.5868
2	15.130	M	0.8633	77357	2243	0.4132

(*R*)-N-((3-fluorophenyl)carbamothioyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3af)

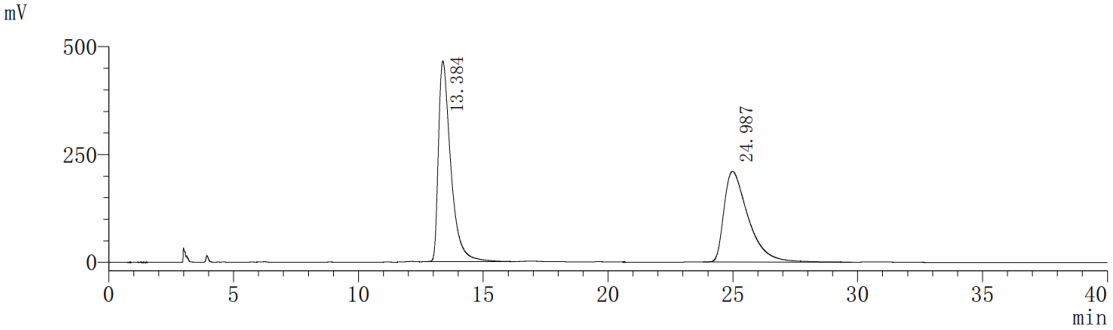


The title compound **3af** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3af** was obtained as a light yellow oil (36.3 mg, 80%). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.16 (s, 1H), 9.87 (s, 1H), 8.26 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.23 – 7.17 (m, 3H), 7.06 – 7.04 (m, 2H), 6.96 (td, *J* = 8.2, 2.4 Hz, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.79, 177.47, 167.16, 162.53 (d, *J* = 244.6 Hz), 143.71, 141.84, 139.28, 138.91 (d, *J* = 10.4 Hz), 135.42, 133.93, 133.23, 132.03, 131.45, 131.25, 131.04, 130.29, 130.00 (d, *J* = 9.1 Hz), 129.39, 128.46, 128.38, 128.17, 127.68, 119.20 (d, *J* = 3.2 Hz), 113.61 (d, *J* = 21.2 Hz), 111.04 (d, *J* = 25.7 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -110.95 – -110.99 (m, 1F).

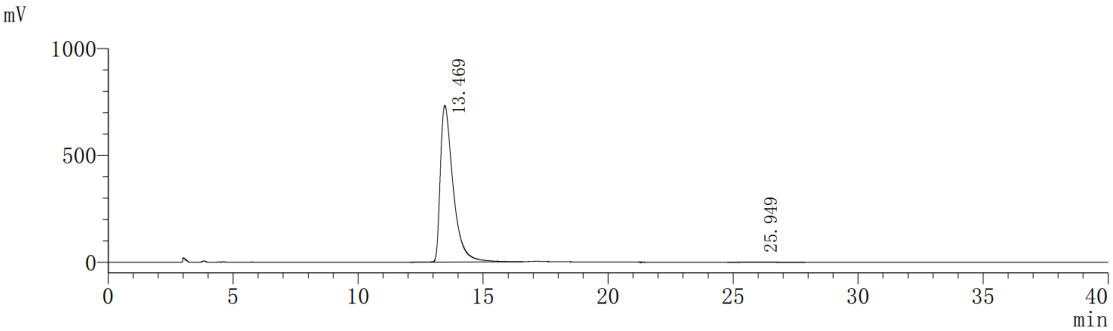
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{19}FN_2NaO_2S$, ($[M + Na]^+$), 477.1043; found 477.1041.

$[\alpha]_D^{20}$ = -106.9 (c = 1.8, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 13.38 min, t_R (minor) = 24.99 min, 99% ee.

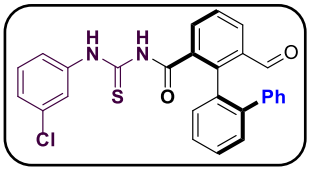


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.384	M	0.8601	16034501	465231	53.1187
2	24.987	M	1.7424	14151686	210107	46.8813



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.469	M	0.8887	26150743	733605	99.5911
2	25.949	M	1.4430	107357	1585	0.4089

(*R*)-*N*-((3-chlorophenyl)carbamothioyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ag)

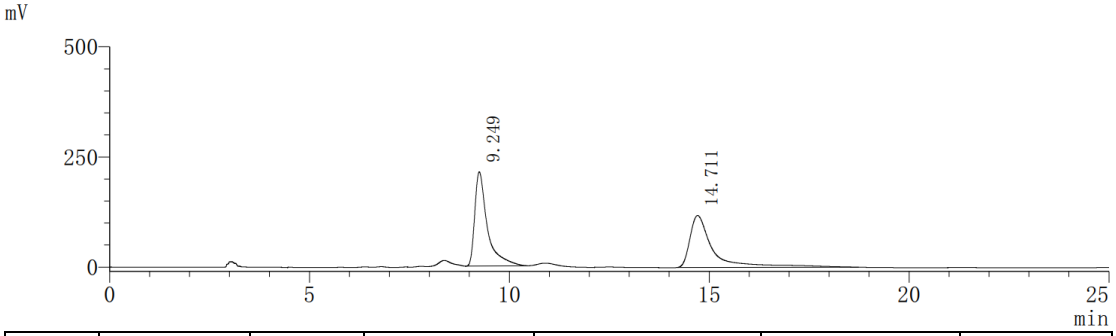


The title compound **3ag**was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 2:1). **3ag** was obtained as a yellow oil (23.5 mg, 50%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.11 (s, 1H), 9.87 (d, *J* = 0.8 Hz, 1H), 8.28 (s, 1H), 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.81 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.77 (t, *J* = 2.1 Hz, 1H), 7.63 (td, *J* = 7.5, 1.4 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.51 – 7.49 (m, 1H), 7.38 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.18 (m, 4H), 7.06 – 7.04 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.95, 177.85, 167.34, 143.90, 141.98, 139.45, 138.73, 135.57, 134.59, 134.09, 133.36, 132.20, 131.60, 131.40, 131.19, 130.44, 129.99, 129.54, 128.61, 128.53, 128.31, 127.82, 127.04, 124.05, 122.11.

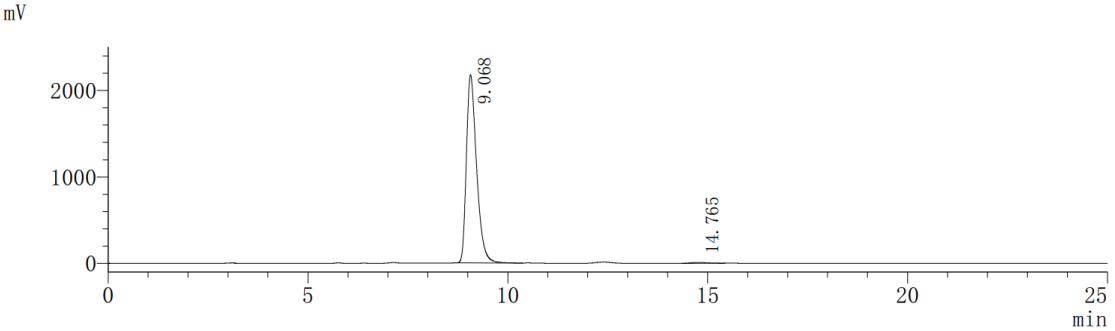
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{20}ClN_2O_2S$, ($[M + Na]^+$), 471.0929; found 471.0944.

$[\alpha]_D^{20}$ = -14.8 (c = 1.2, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 9.07 min, t_R (minor) = 14.77 min, 99% ee.

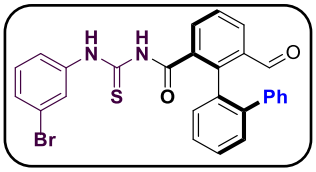


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	9.249	M	0.5007	4696410	213954	49.5399
2	14.711	M	0.8378	4783646	117950	50.4601



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	9.068	M	0.4604	38555800	2173537	99.3083
2	14.765	M	0.7406	268543	9925	0.6917

(*R*)-*N*-((3-bromophenyl)carbamothioyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ah)

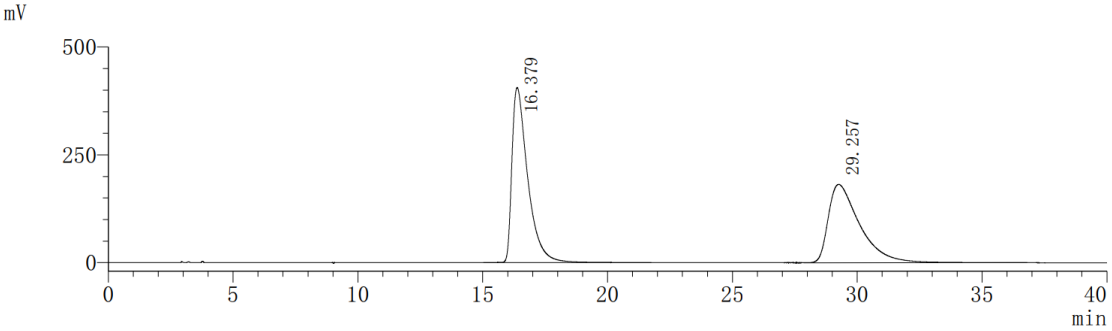


The title compound **3ah** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ah** was obtained as a white solid (34.4 mg, 67%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.10 (s, 1H), 9.86 (s, 1H), 8.29 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.90 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.64 – 7.54 (m, 5H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.26 – 7.18 (m, 4H), 7.05 (d, *J* = 7.1 Hz, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.95, 177.88, 167.46, 143.94, 141.97, 139.45, 138.78, 135.50, 134.06, 133.38, 132.23, 131.56, 131.38, 131.13, 130.39, 130.26, 129.98, 129.54, 128.61, 128.48, 128.28, 127.81, 126.93, 122.65, 122.40.

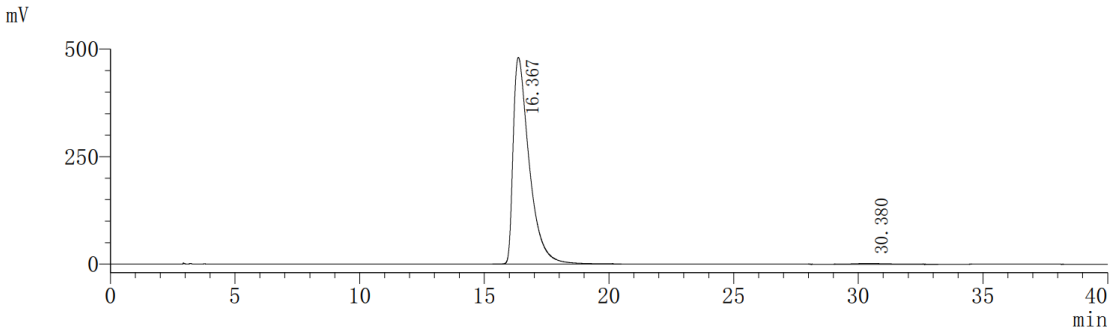
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{19}BrN_2NaO_2S$, ($[M + Na]^+$), 537.0243; found 537.0236.

$[\alpha]_D^{20}$ = -35.5 (c = 1.7, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 16.37 min, t_R (minor) = 30.38 min, 99% ee.

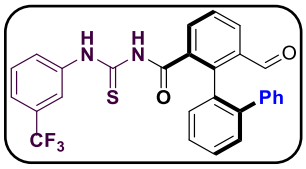


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	16.379	M	1.1185	17938950	406188	52.9882
2	29.257	M	2.2414	15915675	181607	47.0118



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	16.367	M	1.1291	21555107	480854	99.2874
2	30.380	M	1.9296	154712	1633	0.7126

(*R*)-6-formyl-*N*-((3-(trifluoromethyl)phenyl)carbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ai)

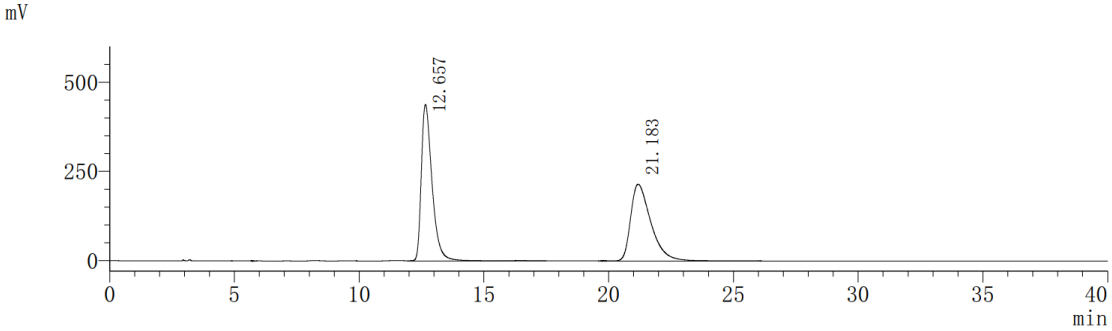


The title compound **3ai** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ai** was obtained as a white solid (33.8 mg, 67%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.22 (s, 1H), 9.87 (s, 1H), 8.31 (s, 1H), 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.96 (s, 1H), 7.88 – 7.86 (m, 1H), 7.83 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.60 – 7.55 (m, 3H), 7.52 – 7.51 (m, 2H), 7.39 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.23 – 7.18 (m, 3H), 7.07 – 7.05 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.89, 178.08, 167.42, 143.88, 142.01, 139.46, 138.20, 135.61, 134.02, 133.41, 132.21, 131.66, 131.53 (q, *J* = 32.6 Hz), 131.38, 131.23, 130.48, 129.55, 129.54, 128.62, 128.56, 128.35, 127.85, 127.18, 123.81 (q, *J* = 270.7 Hz), 123.51 (q, *J* = 3.9 Hz), 120.86 (q, *J* = 4.0 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -62.74 (s, 1CF_3).

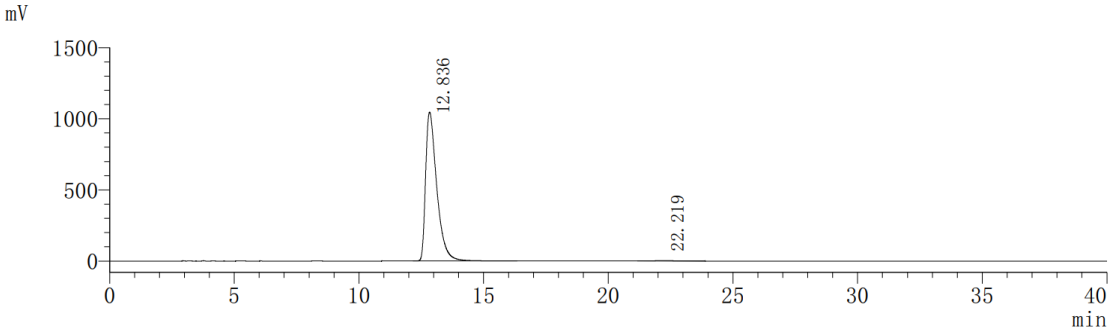
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{20}F_3N_2O_2S$, ([M + Na]$^+$), 505.1192; found 505.1206.

$[\alpha]_D^{20}$ = -89.4 (c = 1.7, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 12.84 min, t_R (minor) = 22.22 min, 99% ee.

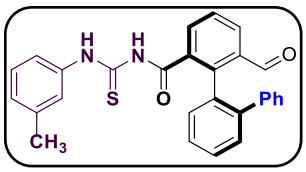


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	12.657	M	0.7572	13252027	439482	52.1832
2	21.183	M	1.4552	12143173	215242	47.8168



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	12.836	M	0.7858	32526443	1046406	99.4622
2	22.219	M	1.6746	175876	2876	0.5378

(*R*)-6-formyl-*N*-(m-tolylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3aj)

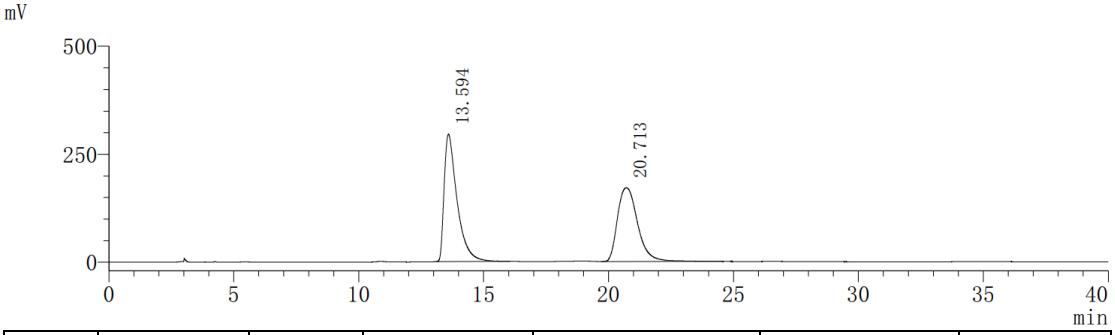


The title compound **3aj** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3aj** was obtained as a yellow solid (32.9 mg, 73%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.00 (s, 1H), 9.86 (s, 1H), 8.28 (s, 1H), 8.12 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.81 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.61 (td, *J* = 7.5, 1.4 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.46 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.41 (s, 1H), 7.38 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.22 – 7.18 (m, 3H), 7.08 – 7.06 (m, 3H), 2.37 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.96, 177.66, 167.22, 143.88, 142.02, 139.52, 139.03, 137.53, 135.52, 134.36, 133.25, 132.32, 131.38, 131.36, 131.10, 130.31, 129.55, 128.83, 128.58, 128.46, 128.23, 127.82, 127.76, 124.60, 121.15, 21.54.

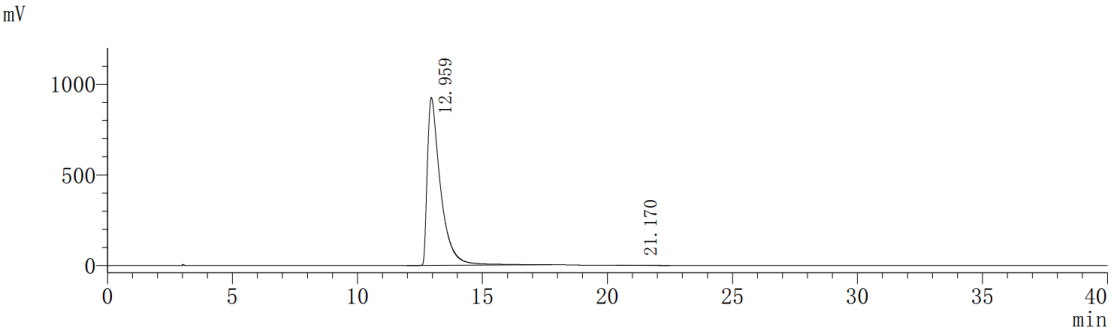
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}N_2NaO_2S$, ($[M + Na]^+$), 473.1294; found 473.1296.

$[\alpha]_D^{20}$ = -135.4 (c = 1.6, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 12.96 min, t_R (minor) = 21.17 min, 99% ee.

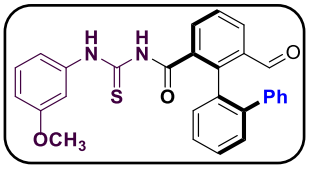


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	13.594	M	0.9222	10607005	295017	52.3546
2	20.713	M	1.3782	9652927	171073	47.6454



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	12.959	M	0.9001	34177444	926084	99.8347
2	21.170	M	1.5465	56590	891	0.1653

(*R*)-6-formyl-*N*-((3-methoxyphenyl)carbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ak)

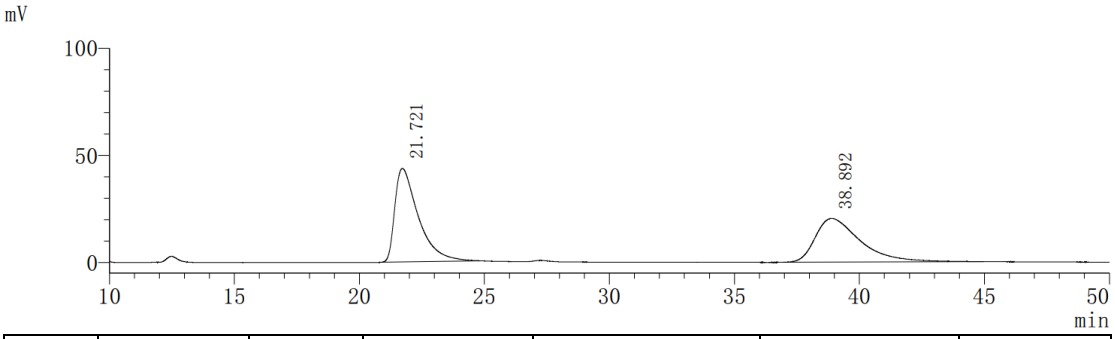


The title compound **3ak** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ak** was obtained as a light yellow oil (23.8 mg, 51%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.07 (s, 1H), 9.87 (d, *J* = 0.9 Hz, 1H), 8.19 (s, 1H), 8.14 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.82 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.59 – 7.54 (m, 3H), 7.42 – 7.38 (m, 2H), 7.29 (t, *J* = 8.2 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.14 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.07 – 7.05 (m, 2H), 6.82 – 6.80 (m, 1H), 3.82 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.99, 177.46, 167.20, 160.11, 143.89, 142.05, 139.51, 138.77, 135.63, 134.31, 133.34, 132.28, 131.52, 131.44, 131.21, 130.43, 129.75, 129.59, 128.63, 128.54, 128.32, 127.83, 116.12, 112.83, 109.54, 55.64.

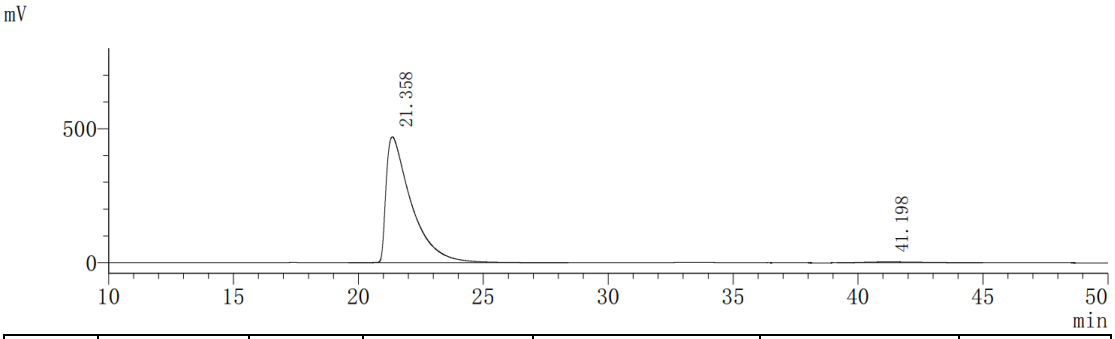
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}N_2NaO_3S$, ($[M + Na]^+$), 489.1243; found 489.1228.

$[\alpha]_D^{20}$ = -68.3 (c = 1.2, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 21.36 min, t_R (minor) = 41.20 min, 97% ee.

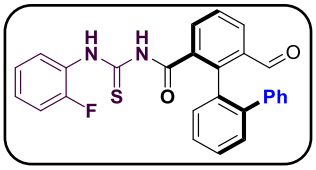


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	21.721	M	1.6724	2857627	43698	52.7018
2	38.892	M	3.1575	2564627	20438	47.2982



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	21.358	M	1.7719	33130048	470191	98.4097
2	41.198	M	3.9330	535388	3232	1.5903

(*R*)-*N*-((2-fluorophenyl)carbamothioyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3al)

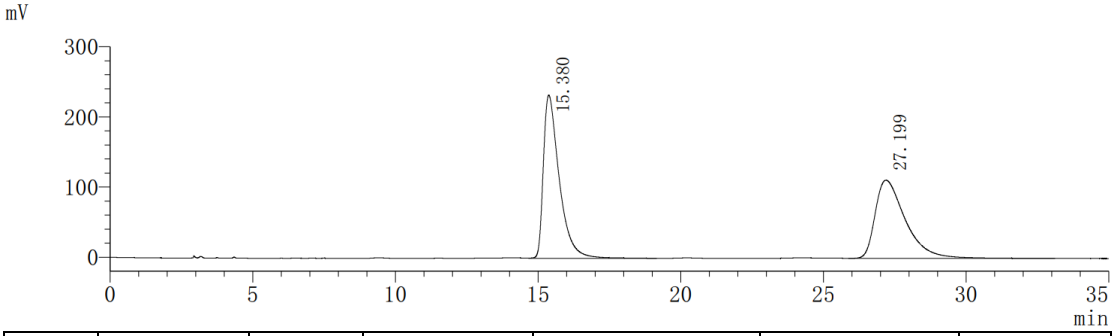


The title compound **3al** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3al** was obtained as a yellow oil (29.5 mg, 65%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.03 (s, 1H), 9.91 (s, 1H), 8.27 (s, 1H), 8.18 – 8.15 (m, 2H), 7.83 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.64 – 7.54 (m, 4H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.14 (m, 6H), 7.06 – 7.05 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.04, 178.48, 167.10, 155.44 (d, *J* = 247.2 Hz), 143.82, 142.11, 139.43, 135.62, 134.10, 133.61, 132.17, 131.54 (d, *J* = 13.2 Hz), 131.26, 130.48, 129.59, 128.64, 128.50, 128.32, 128.13 (d, *J* = 7.8 Hz), 127.79, 126.06, 125.93 (d, *J* = 10.9 Hz), 124.19 (d, *J* = 3.6 Hz), 115.88 (d, *J* = 19.5 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -124.11 – -124.15 (m, 1F).

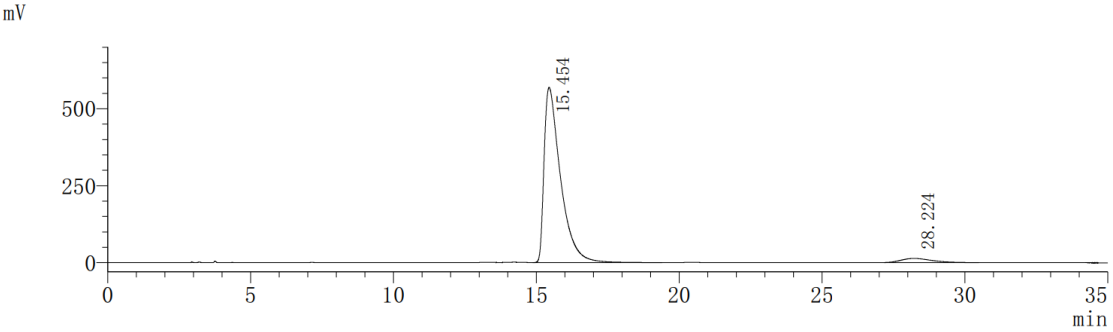
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{20}FN_2O_2S$, ($[M + H]^+$), 455.1224; found 455.1220.

$[\alpha]_D^{20}$ = -95.2 (c = 1.5, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 15.45 min, t_R (minor) = 28.22 min, 92% ee.

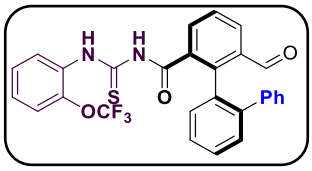


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.380	M	0.9705	9013777	232632	52.2277
2	27.199	M	1.8702	8244847	111586	47.7723



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	15.454	M	1.0135	22762472	568843	95.7789
2	28.224	M	1.9663	1003183	13459	4.2211

(*R*)-6-formyl-*N*-((2-(trifluoromethoxy)phenyl)carbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3am)

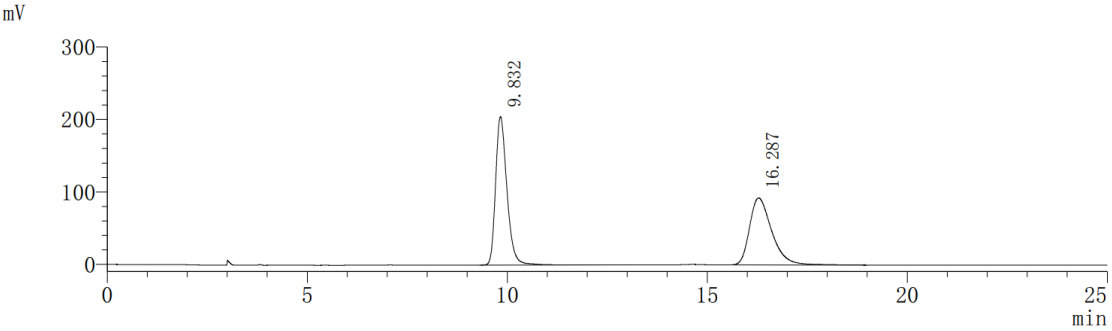


The title compound **3am** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3am** was obtained as a light yellow oil (27.0 mg, 52%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.35 (s, 1H), 9.93 (s, 1H), 8.48 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.26 (s, 1H), 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.58 – 7.53 (m, 3H), 7.40 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 7.22 – 7.16 (m, 3H), 7.05 – 7.03 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.06, 178.08, 167.10, 143.91, 142.08, 141.40, 139.52, 135.57, 134.17, 133.57, 132.21, 131.48, 131.34, 131.20, 130.76, 130.39, 129.50, 128.60, 128.49, 128.27, 127.72, 127.41, 127.01, 125.65, 121.20, 120.6 (q, *J* = 257.9 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -57.75 (s, 1OCF_3).

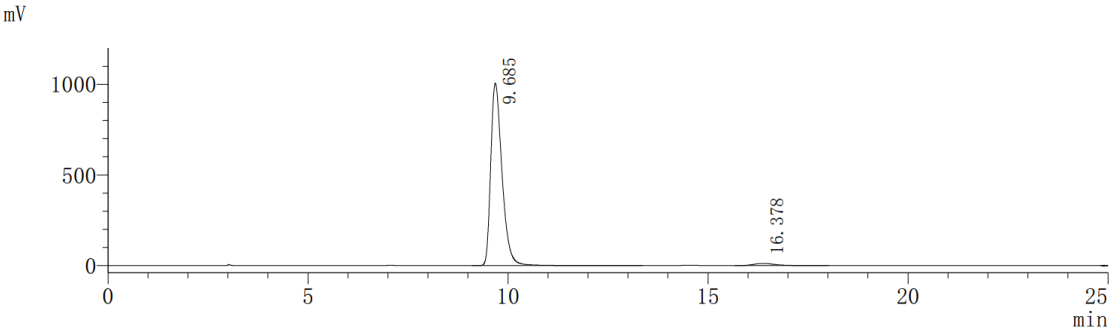
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{20}F_3N_2O_3S$, ([M + Na]$^+$), 521.1141; found 521.1133.

$[\alpha]_D^{20}$ = -84.0 (c = 1.4, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 9.69 min, t_R (minor) = 16.38 min, 95% ee.

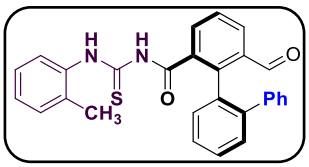


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	9.832	M	0.5053	4043025	204779	53.0842
2	16.287	M	0.9953	3573225	92472	46.9158



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	9.685	M	0.5037	19752877	1006264	97.7101
2	16.378	M	0.9943	462928	11777	2.2899

(*R*)-6-formyl-*N*-(o-tolylcarbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3an)

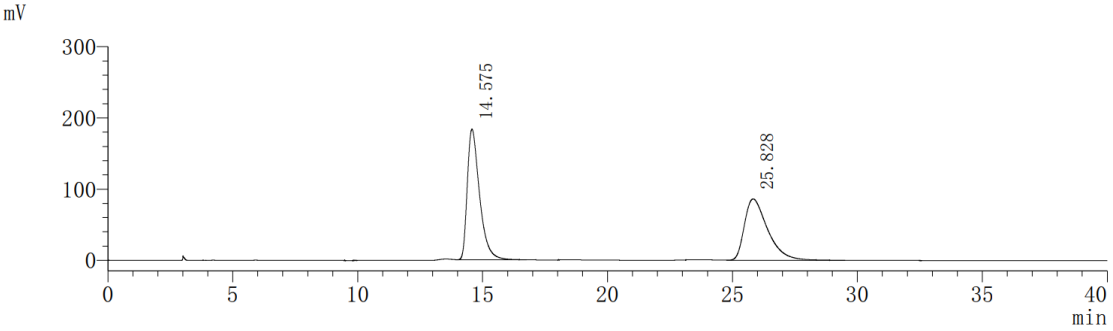


The title compound **3an** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3an** was obtained as a yellow solid (25.2 mg, 56%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 11.72 (s, 1H), 9.90 (d, *J* = 0.9 Hz, 1H), 8.33 (s, 1H), 8.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.59 – 7.54 (m, 3H), 7.40 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.27 – 7.18 (m, 6H), 7.09 – 7.07 (m, 2H), 2.27 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.00, 178.87, 167.31, 143.87, 142.04, 139.55, 136.39, 135.55, 134.42, 133.37, 133.29, 132.38, 131.40, 131.34, 131.12, 130.94, 130.37, 129.56, 128.60, 128.50, 128.23, 127.84, 127.78, 126.64, 126.22, 18.10.

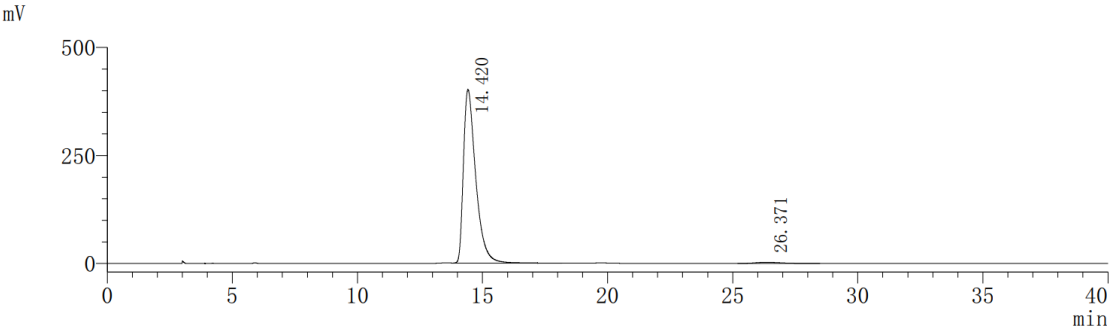
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}N_2NaO_2S$, ($[M + Na]^+$), 473.1294; found 473.1302.

$[\alpha]_D^{20}$ = -95.3 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 14.42 min, t_R (minor) = 26.37 min, 97% ee.

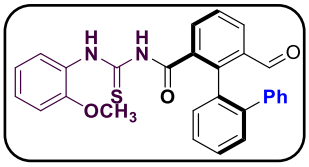


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.575	M	0.8721	6255344	183385	52.8318
2	25.828	M	1.6828	5584765	86295	47.1682



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	14.420	M	0.8690	13723104	401736	98.5413
2	26.371	M	1.7363	203149	2839	1.4587

(*R*)-6-formyl-*N*-((2-methoxyphenyl)carbamothioyl)-[1,1':2',1''-terphenyl]-2-carboxamide (3ao)

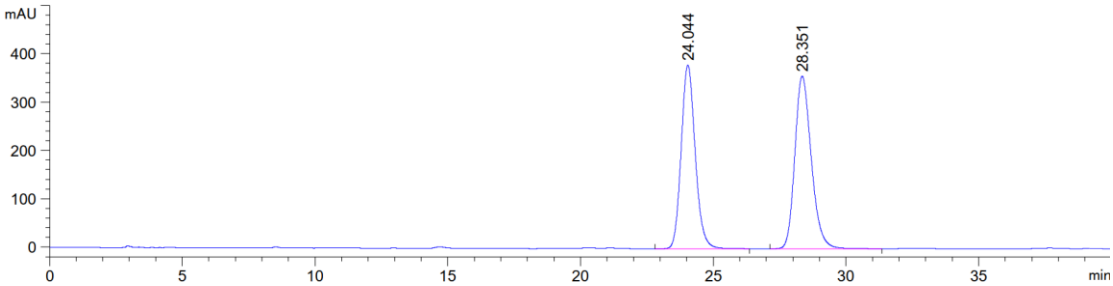


The title compound **3ao** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ao** was obtained as a yellow oil (29.4 mg, 63%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.22 (s, 1H), 9.84 (d, *J* = 0.8 Hz, 1H), 8.50 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.12 (s, 1H), 8.07 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.77 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.51 – 7.46 (m, 3H), 7.34 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.16 – 7.10 (m, 4H), 7.01 – 6.99 (m, 2H), 6.93 (td, *J* = 7.8, 1.3 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.81 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.10, 176.48, 166.59, 151.04, 143.71, 142.16, 139.54, 135.50, 134.52, 133.55, 132.33, 131.47, 131.28, 131.17, 130.29, 129.61, 128.56, 128.45, 128.28, 127.68, 127.22, 127.05, 123.49, 120.39, 110.87, 56.08.

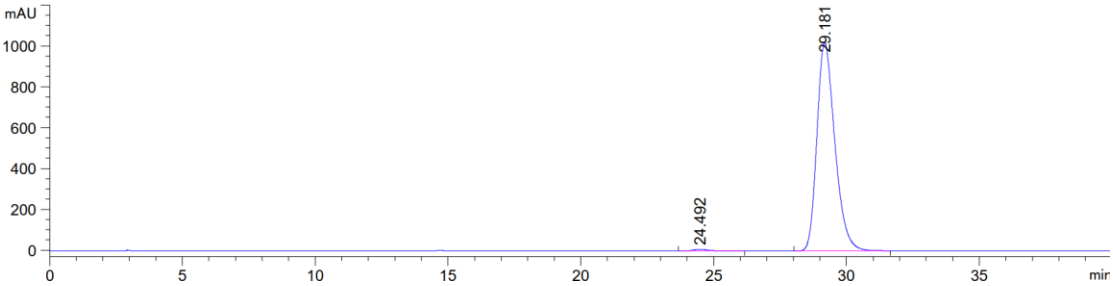
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}N_2NaO_3S$, ($[M + Na]^+$), 489.1243; found 489.1246.

$[\alpha]_D^{20}$ = -108.8 (c = 1.5, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 24.49 min, t_R (minor) = 29.18 min, 99% ee.

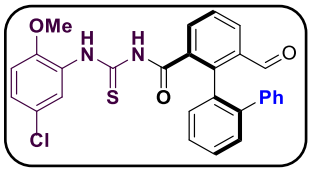


Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	24.044	MM	0.5657	1.39214e4	379.76120	47.5584
2	28.351	MM	0.6598	1.53508e4	356.90024	52.4416



Peak	Pet Time	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	24.492	MM	0.6261	360.05847	8.64218	0.7473
2	29.181	MM	0.7237	4.78238e4	1018.71906	99.2527

(*R*)-*N*-((5-chloro-2-methoxyphenyl)carbamothioyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3ap)

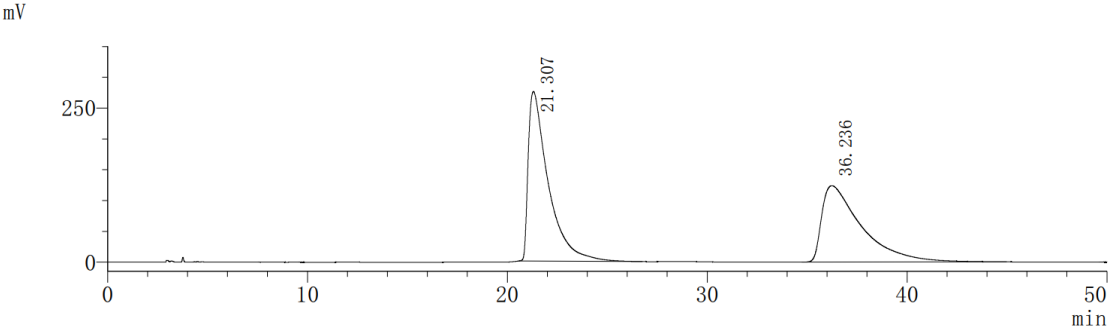


The title compound **3ap** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3ap** was obtained as a yellow oil (39.5 mg, 79%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.38 (s, 1H), 9.89 (s, 1H), 8.78 (d, *J* = 2.5 Hz, 1H), 8.20 (s, 1H), 8.13 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.83 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.58 – 7.53 (m, 3H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.22 – 7.13 (m, 4H), 7.04 – 7.03 (m, 2H), 6.84 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 191.01, 176.37, 166.63, 149.37, 143.63, 142.12, 139.46, 135.50, 134.27, 133.64, 132.23, 131.44, 131.41, 131.21, 130.35, 129.56, 128.55, 128.47, 128.32, 128.18, 127.68, 126.28, 125.33, 122.78, 111.60, 56.40.

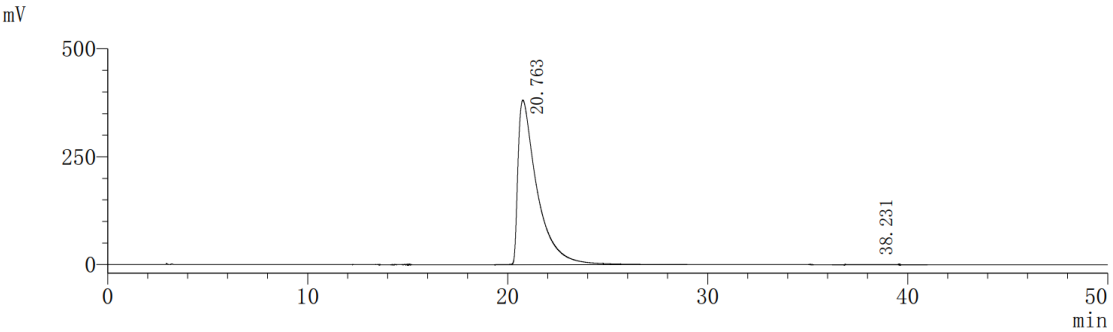
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{21}ClN_2NaO_3S$, ($[M + Na]^+$), 523.0854; found 523.0847.

$[\alpha]_D^{20}$ = -96.5 (c = 1.9, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-H column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 20.76 min, t_R (minor) = 38.23 min, 99% ee.

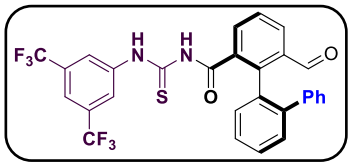


Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	21.307	M	1.7305	19250524	275201	52.9101
2	36.236	M	3.4683	17132932	123945	47.0899



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	20.763	M	1.6351	25434112	381072	99.8861
2	38.231	M	1.9049	28995	218	0.1139

(*R*)-*N*-((3,5-bis(trifluoromethyl)phenyl)carbamothioyl)-6-formyl-[1,1':2',1''-terphenyl]-2-carboxamide (3aq)

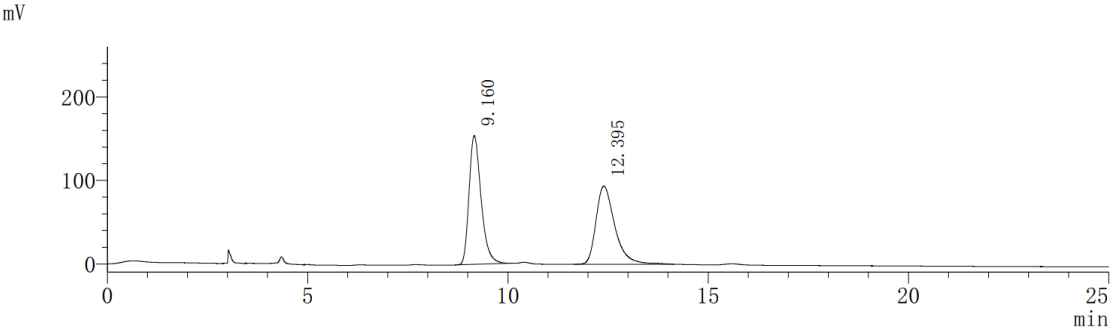


The title compound **3aq** was prepared under the optimized conditions A and purified by preparative TLC (hexane: ethyl acetate = 10:3). **3aq** was obtained as a white solid (23.5 mg, 41%). **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.44 (s, 1H), 9.88 (s, 1H), 8.32 (s, 1H), 8.22 (s, 2H), 8.17 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.75 (s, 1H), 7.67 – 7.64 (m, 1H), 7.61 – 7.57 (m, 3H), 7.41 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.24 – 7.18 (m, 3H), 7.05 (dd, *J* = 8.1, 1.6 Hz, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 190.81, 178.23, 167.58, 143.87, 142.02, 139.39, 139.16, 135.72, 133.71, 133.56, 132.46 (q, *J* = 33.5 Hz), 132.10, 131.93, 131.38, 131.37, 130.64, 129.53, 128.68, 128.67, 128.47, 127.95, 123.75 (q, *J* = 3.9 Hz), 123.09 (q, *J* = 271.1 Hz), 120.15 (p, *J* = 3.8 Hz). **^{19}F NMR (565 MHz, Chloroform-*d*)** δ -63.00 (s, 2CF_3).

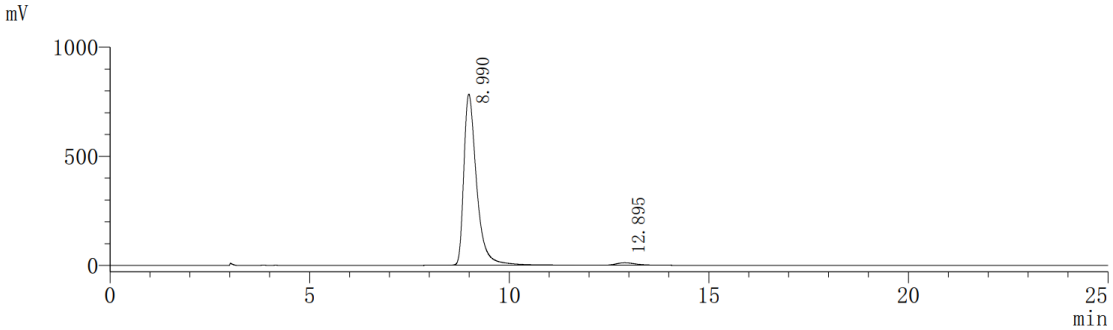
HRMS (ESI-TOF) (m/z): Calcd for $C_{29}H_{18}F_6N_2NaO_2S$, ([M + Na]$^+$), 595.0885; found 595.0879.

$[\alpha]_D^{20}$ = -77.5 (c = 1.2, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (major) = 8.99 min, t_R (minor) = 12.90 min, 96% ee.



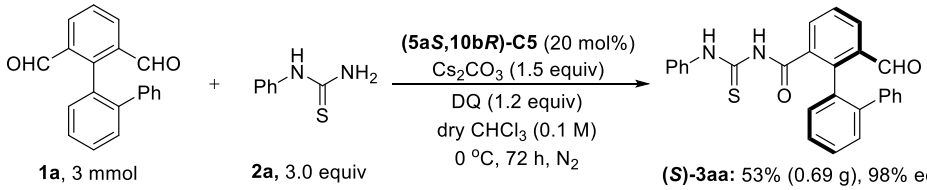
Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	9.160	M	0.5397	3238625	154375	51.3867
2	12.395	M	0.8273	3063828	93682	48.6133



Peak	Pet Time	Type	Width(min)	Area	Hight	Area%
1	8.990	M	0.5524	17437157	783788	97.8201
2	12.895	M	0.8762	388582	11386	2.1799

III Synthetic Applications

3.1 Scale-up synthesis:

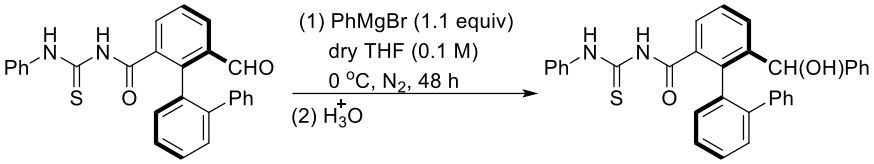


1a, 3 mmol **2a,** 3.0 equiv **(*S*)-3aa:** 53% (0.69 g), 98% ee.

In a nitrogen-filled glovebox, a flame-dried 100 mL Schlenk reaction tube equipped with a magnetic stir bar was charged with **(5a*S*,10b*R*)-C5** (20 mol%, 0.298 g), Cs_2CO_3 (1.466g, 4.5 mmol), [1,1':2',1"-terphenyl]-2,6-dicarbaldehyde **1a** (0.858 g, 3 mmol) and anhydrous chloroform (30.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (1.368 g, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (1.469 g, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 72 h. The mixture was concentrated under reduced pressure and purified by *via* column chromatography on silica gel (hexanes/EtOAc = 10:3) to afford 0.69 g product **3aa** in 53% yield with 98% ee.

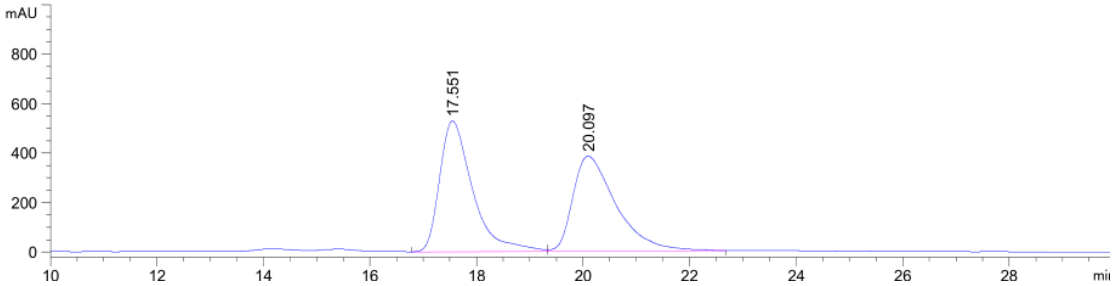
3.2 Synthetic Transformation

3.2.1,

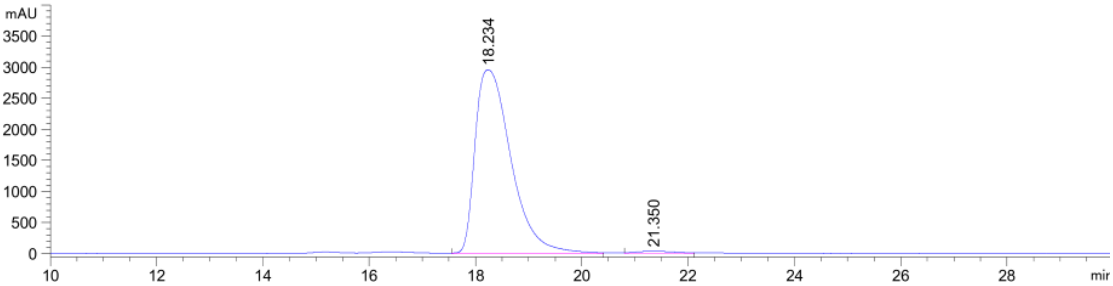


3aa: 0.1 mmol **6a**: 62%, 98% ee (>20:1 dr)

In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **3aa** (0.1 mmol, 43.6 mg) and anhydrous tetrahydrofuran (1.0 mL) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. 1 mol/L PhMgBr in THF (110 μL, 1.1 equiv) was added dropwise and stirring at 0 °C for 48 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3×5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 10:3) to afford the desired product **6a** as a colorless oil. (yield: 62%, 97% ee). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.13 (s, 1H), 8.63 (s, 1H), 7.62 – 7.58 (m, 5H), 7.52 (td, *J* = 7.4, 1.4 Hz, 1H), 7.42 – 7.33 (m, 6H), 7.29 – 7.26 (m, 3H), 7.24 – 7.21 (m, 3H), 7.20 – 7.17 (m, 1H), 7.10 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.04 – 7.03 (m, 2H), 5.57 (d, *J* = 2.6 Hz, 1H), 1.31 (d, *J* = 3.2 Hz, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 178.06, 168.91, 143.87, 142.89, 140.80, 140.26, 138.65, 137.52, 135.26, 133.73, 131.78, 130.53, 130.37, 129.52, 129.24, 128.82, 128.48, 128.44, 128.34, 128.10, 127.55, 127.38, 127.00, 126.83, 126.07, 124.12, 71.52.
HRMS (ESI-TOF) (m/z): Calcd for $C_{33}H_{26}N_2NaO_2S$, ($[M + Na]^+$), 537.1607; found 537.1615.
$[\alpha]_D^{19}$ = -14.4 (c = 1.6, CH_2Cl_2).
HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 210 nm); t_R (major) = 18.23 min, t_R (minor) = 21.35 min, 98% ee.

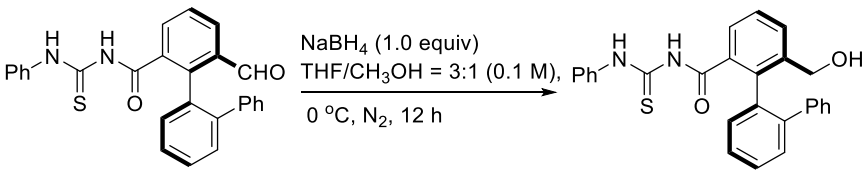


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	17.551	M	0.6443	2.26402e4	527.92566	51.2619
2	20.097	M	0.8641	2.15255e4	383.94266	48.7381



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	18.234	M	0.7842	1.38932e5	2952.62573	98.7900
2	21.350	M	0.8423	1701.69006	33.67229	1.2100

3.2.2,



3aa: 0.1 mmol

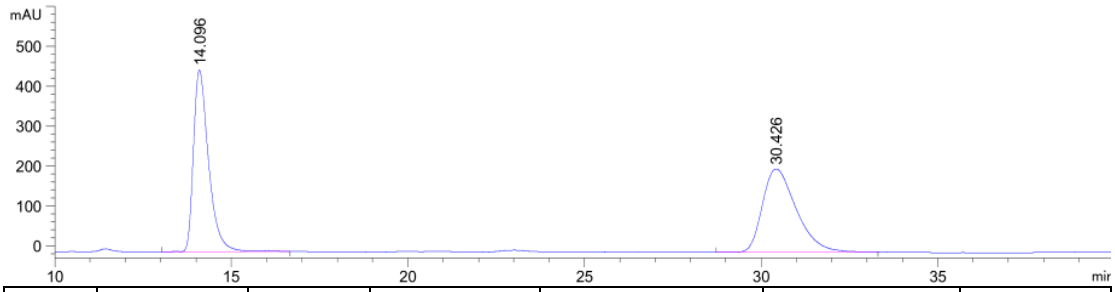
6b: 66%, 97% ee

In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **3aa** (0.1 mmol, 43.6 mg), $NaBH_4$ (0.1 mmol, 3.8 mg) and dry THF/CH_3OH = 3:1 (1.0 mL) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. Reaction mixture was stirred at 0 °C for 12 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3×5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 1:1) to give the desired product **6b** as a colorless oil. (yield: 66%, 97% ee). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.12 (s, 1H), 8.39 – 8.36 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.53 (m, 3H), 7.51 – 7.48 (m, 1H), 7.45 – 7.42 (m, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 – 7.19 (m, 3H), 7.13 – 7.12 (m, 2H), 4.47 (d, *J* = 13.5 Hz, 1H), 4.38 (d, *J* = 13.5 Hz, 1H), 1.59 (s, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 178.09, 168.46, 140.89, 140.58, 139.93, 138.77, 137.56, 134.86, 133.34, 131.70, 130.79, 129.85, 129.35, 129.19, 128.84, 128.25, 128.17, 128.07, 127.41, 127.14, 126.81, 124.12, 62.66.

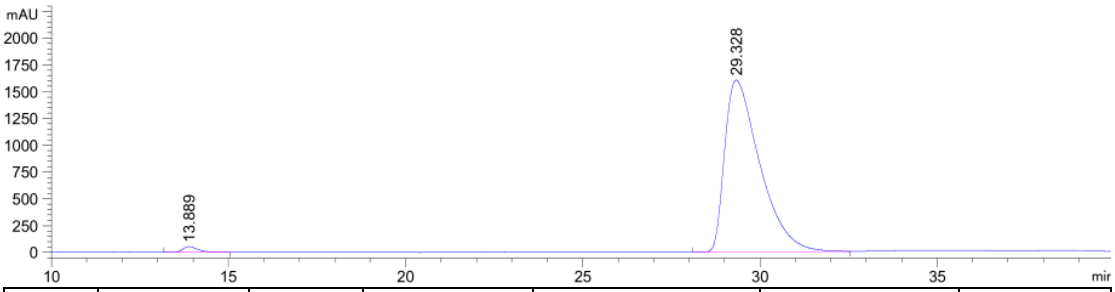
HRMS (ESI-TOF) (m/z): Calcd for $C_{27}H_{22}N_2NaO_2S$, ($[M + Na]^+$), 461.1294; found 461.1297.

$[\alpha]_D^{19}$ = +61.2 (c = 1.4, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (90:10 hexane: 2-propanol, 1.0 mL/min, 25 °C, 210 nm); t_R (minor) = 13.89 min, t_R (major) = 29.33 min, 97% ee.

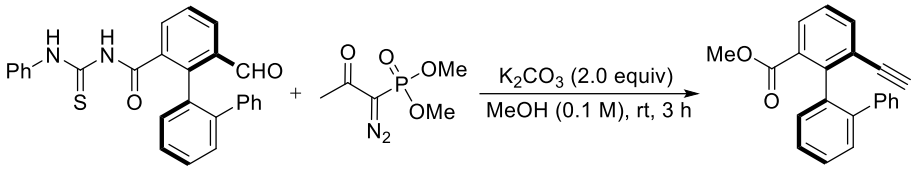


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.096	M	0.4496	1.36684e4	454.95319	49.5241
2	30.426	M	0.9998	1.39311e4	208.95663	50.4759



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	13.889	M	0.4609	1650.64404	54.11298	1.4733
2	29.328	M	1.0359	1.10384e5	1603.98682	98.5267

3.2.3,



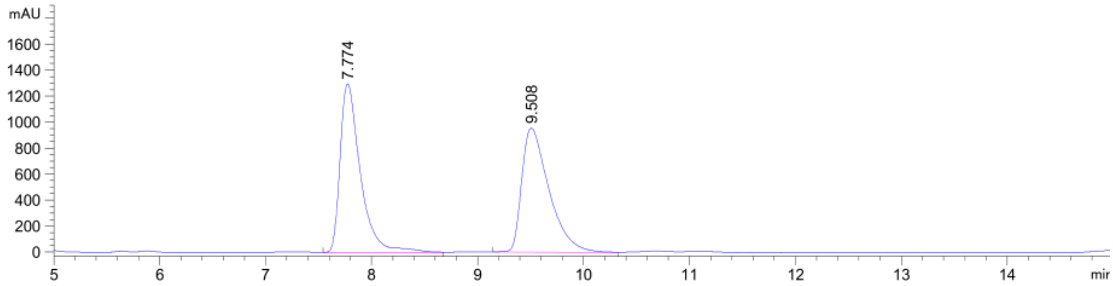
3aa: 0.1 mmol 1.5 equiv **6c**: 93%, 93% ee

To a solution of **3aa** (0.1 mmol, 43.6 mg) in 1.0 mL MeOH was added K_2CO_3 (0.2 mmol, 27.6 mg), P-(1-diazo-2-oxopropyl)-dimethylester (0.15 mmol, 22.5 µL) is slowly added. the reaction mixture was stirred at rt for 3 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3×5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 10 : 3) to give the desired **6c** (yield: 93%, 93% ee). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 7.70 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.28 – 7.24 (m, 2H), 7.14 (s, 5H), 3.55 (s, 3H), 2.94 (s, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 167.25, 145.14, 141.13, 140.98, 137.82, 135.94, 131.90, 130.00, 129.75, 129.54, 129.45, 127.98, 127.52, 126.93, 126.72, 126.57, 124.07, 82.15, 81.49, 52.01.

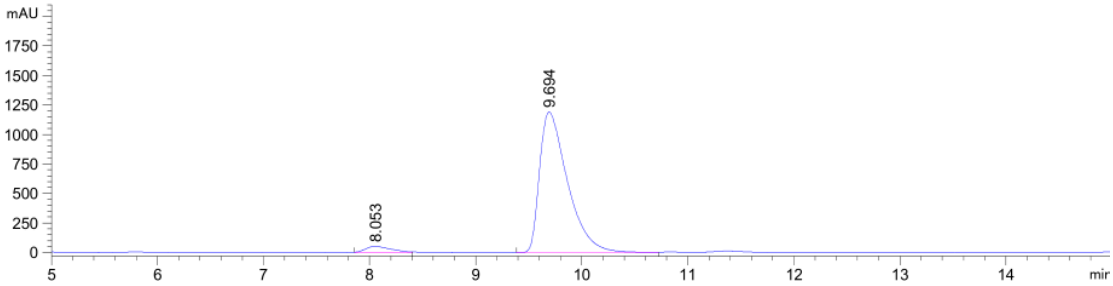
HRMS (ESI-TOF) (m/z): Calcd for $C_{22}H_{16}NaO_2$, ([M + Na]$^+$), 335.1043; found 335.1041.

[α]$_D^{19}$ = -46.2 (c = 1.3, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 210 nm); t_R (minor) = 8.05 min, t_R (major) = 9.69 min, 93% ee.

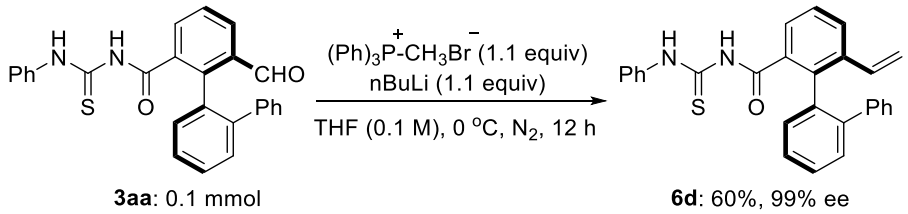


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	7.774	M	0.2217	1.72696e4	1298.02734	50.4089
2	9.508	M	0.2971	1.69894e4	953.02484	49.5911



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	8.053	M	0.2667	811.93359	50.73443	3.5703
2	9.694	M	0.3068	2.19294e4	1191.48743	96.4297

3.2.4,



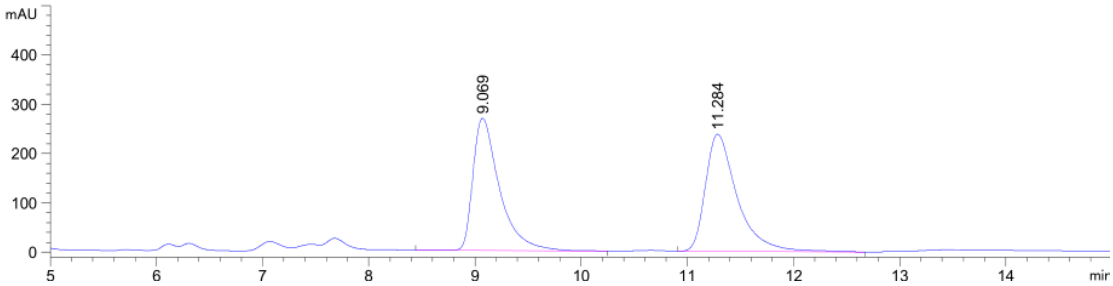
3aa: 0.1 mmol **6d**: 60%, 99% ee

In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with methyltriphenylphosphonium bromide (0.11 mmol, 39.3 mg), anhydrous tetrahydrofuran (0.5 mL) and nBuLi of 2.5 mol/L in hexane (0.11 mmol, 45 μL) was added. Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The mixture was stirred at 0 °C for 30 minutes, followed by tetrahydrofuran solution (0.5 mL) dissolved in **3aa** (0.1 mmol, 43.6 mg) was added dropwise and stirring at 0 °C for 12 h, until the reaction was complete as indicated by TLC. The reaction mixture was then quenched with water, extracted with CH_2Cl_2 (3×5 mL). Drying (Na_2SO_4) and evaporation of the solvent gave a residue that was purified by silica gel column chromatography (PE : EA = 10:3) to give the desired **6d** (yield: 60 %, 99% ee). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.11 (s, 1H), 8.08 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 3H), 7.34 – 7.31 (m, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.16 (m, 3H), 7.05 – 7.03 (m, 2H), 6.61 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.71 (d, *J* = 17.4 Hz, 1H), 5.26 (d, *J* = 10.9 Hz, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 177.99, 168.26, 141.32, 139.98, 138.73, 138.54, 137.64, 135.09, 134.74, 133.55, 131.07, 130.75, 129.37, 129.26, 128.83, 128.11, 127.88, 127.49, 127.25, 126.73, 124.05, 116.71.

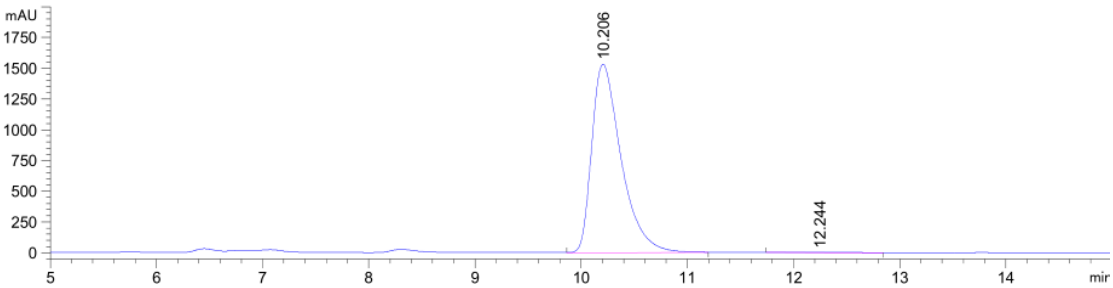
HRMS (ESI-TOF) (m/z): Calcd for $C_{28}H_{22}N_2NaOS$, ([M + Na]$^+$), 457.1345; found 457.1344.

[α]D^{19} = -26.7 (c = 1.4, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 210 nm); t_R (major) = 10.21 min, t_R (minor) = 12.24 min, 99% ee.

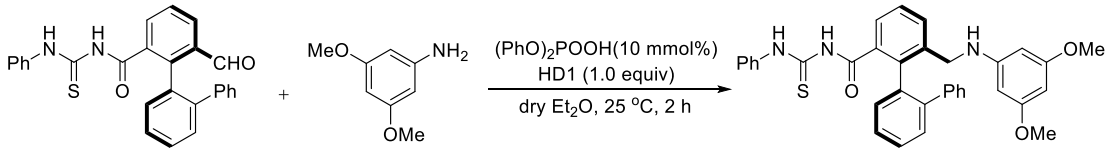


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	9.069	M	0.2605	4679.21387	268.27173	48.6477
2	11.284	M	0.3107	4939.35986	237.45549	51.3523



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	10.206	M	0.3195	2.93789e4	1532.35950	99.8537
2	12.244	M	0.4661	43.03435	1.53870	0.1463

3.2.5,



3aa: 0.1 mmol

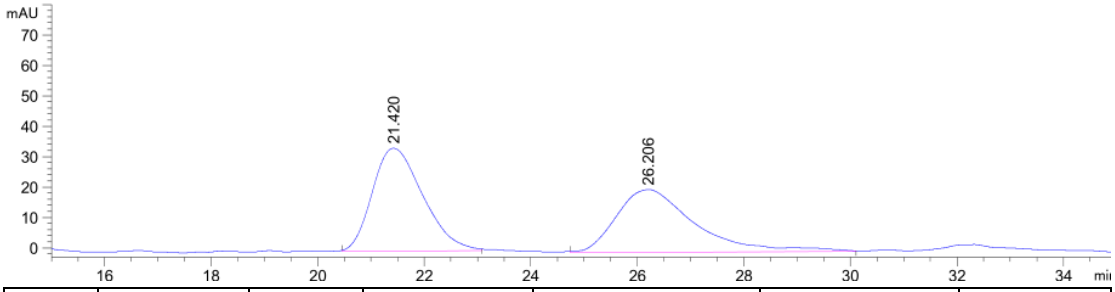
6e: 72%, 99% ee

A 10 mL vial containing a magnetic stir bar, was added **(*S*)-3aa** (43.6 mg, 0.1 mmol, 1.0 equiv), diphenyl phosphate (2.5 mg, 0.01 mmol, 0.1 equiv), Diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate (HD1) (25.4 mg, 0.01 mmol, 1.0 equiv), 3,5-dimethoxyaniline (15.2 mg, 0.1 mmol, 1.0 equiv) and 7.5 ml dry Et_2O. After stirring at the 25 °C for 2 h, the reaction mixture concentrated in vacuo to give a residue, which was purified by flash chromatography to give the desired **6e** (yield: 72%, 99% ee). R_f=0.30 (hexanes/EtOAc = 10:3). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.14 (s, 1H), 8.47 (s, 1H), 7.62 – 7.51 (m, 6H), 7.48 (td, *J* = 7.3, 1.9 Hz, 1H), 7.39 – 7.36 (m, 3H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.17 (m, 6H), 5.85 (s, 1H), 5.56 (d, *J* = 2.1 Hz, 2H), 4.03 (d, *J* = 15.7 Hz, 1H), 3.83 (d, *J* = 15.7 Hz, 1H), 3.69 (s, 6H), 1.57 (s, 1H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 178.08, 168.60, 161.71, 149.56, 140.97, 140.16, 139.47, 139.17, 137.58, 135.18, 133.73, 131.79, 130.82, 129.65, 129.30, 129.18, 128.82, 128.24, 128.15, 128.12, 127.36, 126.79, 126.73, 124.10, 91.85, 89.96, 55.16, 45.90.

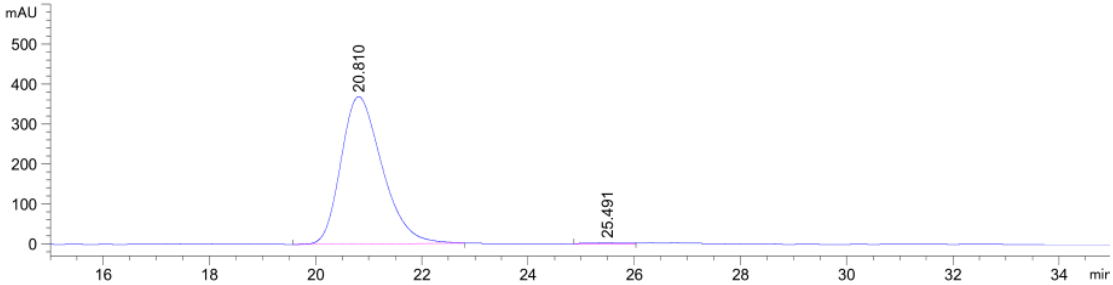
HRMS (ESI-TOF) (m/z): Calcd for $C_{35}H_{31}N_3NaO_3S$, ([M + Na]$^+$), 596.1978; found 596.1968.

$[\alpha]_D^{19}$ = +64.8 (c = 1.5, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 25 °C, 210 nm); t_R (major) = 20.81 min, t_R (minor) = 25.49 min, 99% ee.

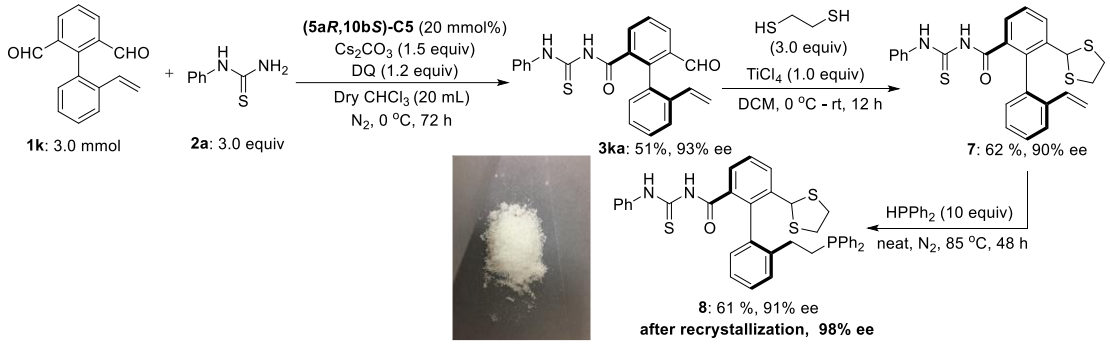


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	21.420	M	1.0983	2231.33032	33.85986	51.4517
2	26.206	M	1.7051	2105.41846	20.57980	48.5483



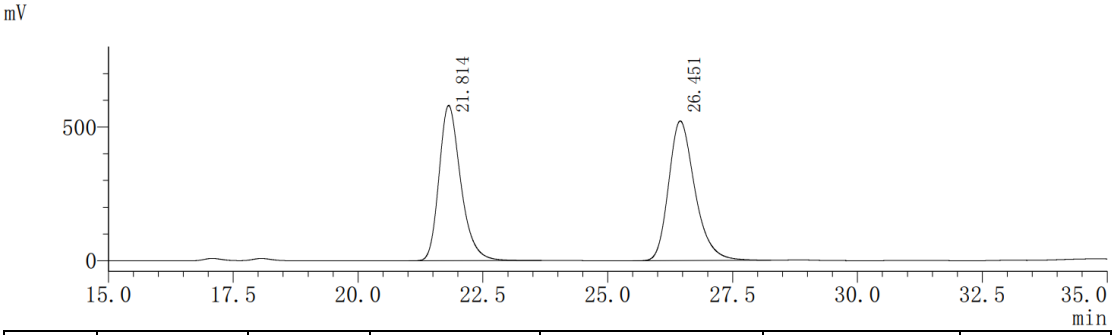
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	20.810	M	0.8293	1.98448e4	368.47266	99.6041
2	25.491	M	0.7105	78.88506	1.85039	0.3959

3.2.6,

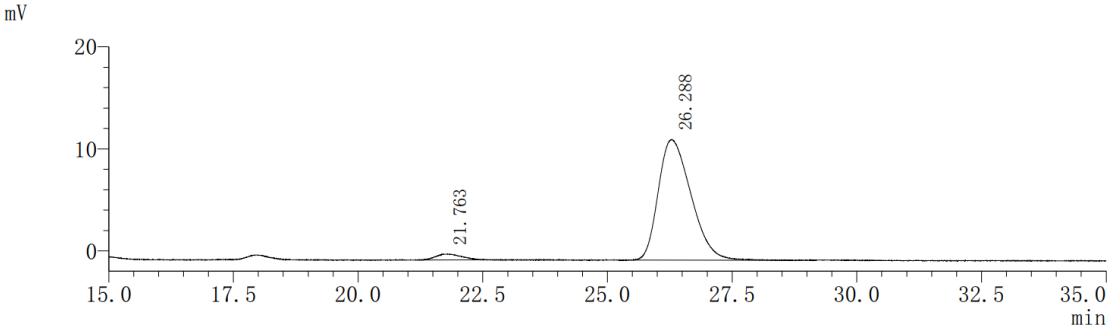


In a nitrogen-filled glovebox, a flame-dried 100 mL Schlenk reaction tube equipped with a magnetic stir bar was charged with **(5a*R*,10b*S*)-C5** (20 mol%, 0.298 g), Cs_2CO_3 (1.466g, 4.5 mmol), 2'-vinyl-[1,1'-biphenyl]-2,6-dicarbaldehyde **1k** (0.708 g, 3 mmol) and anhydrous $CHCl_3$ (20.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (1.368 g, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (1.469 g, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 72 h. The mixture was concentrated under reduced pressure and purified by *via* column chromatography on silica gel (hexanes/EtOAc = 10:3) to afford 0.59 g product (*R*)-**3ka** in 51% yield with 93% ee.

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 21.76 min, t_R (major) = 26.29 min, 93% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	21.814	M	0.7757	17580171	580416	47.8992
2	26.451	M	0.9397	19122252	522116	52.1008



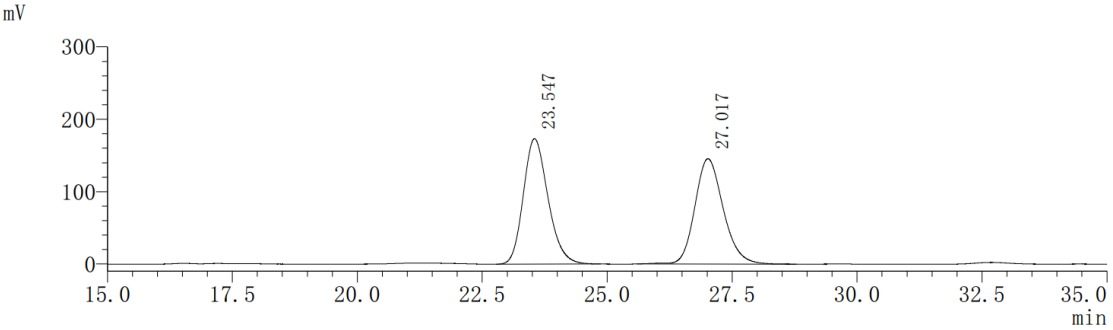
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	21.763	M	0.8225	20744	566	3.7030
2	26.288	M	1.1892	539444	11817	96.2970

Titanium chloride (143 µL, 1.3 mmol) was added to a mixture of (*R*)-**3ka** (0.49 g, 1.3 mmol) and 1,2-ethanedithiol (327 µL, 3.9 mmol) in 5.0 mL CH_2Cl_2 at 0 °C. The mixture was stirred at room temperature for 12 h, then poured into water. The organic layer was washed with water and brine, dried, and concentrated in vacuo. The residue was purification by column chromatography (Petroleum ether/EtOAc = 10:3) gave pure product **7** (white solid, 372 mg, yield: 62%, 90% ee). **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.11 (s, 1H), 8.40 (s, 1H), 8.21 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.72 (td, *J* = 8.7, 1.4 Hz, 2H), 7.58 – 7.55 (m, 3H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.24 – 7.20 (m, 2H), 6.38 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.75 (d, *J* = 17.4 Hz, 1H), 5.30 (s, 1H), 5.28 (d, *J* = 11.1 Hz, 1H), 3.53 – 3.44 (m, 2H), 3.28 – 3.20 (m, 2H). **^{13}C NMR (125 MHz, Chloroform-*d*)** δ 177.72, 168.15, 141.09, 137.66, 137.55, 136.72, 134.42, 133.84, 133.55, 133.00, 129.70, 129.59, 128.90, 128.75, 128.65, 128.21, 126.68, 126.51, 123.96, 117.79, 52.07, 40.64, 40.42.

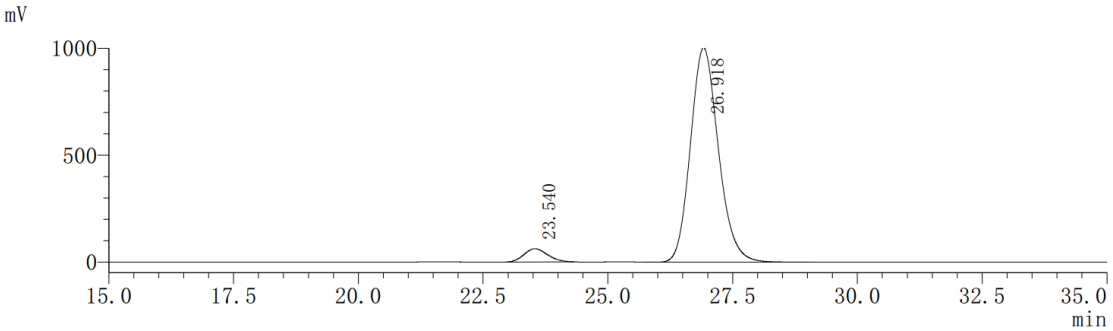
HRMS (ESI-TOF) (m/z): Calcd for $C_{25}H_{22}N_2NaOS_3$, ($[M + Na]^+$), 485.0786; found 485.0786.

$[\alpha]_D^{19}$ = 13.7 (c = 1.0, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak AD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 23.54 min, t_R (major) = 26.92 min, 90% ee.



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.547	M	0.9005	5963759	173375	50.8668
2	27.017	M	1.0245	5760496	145512	49.1332



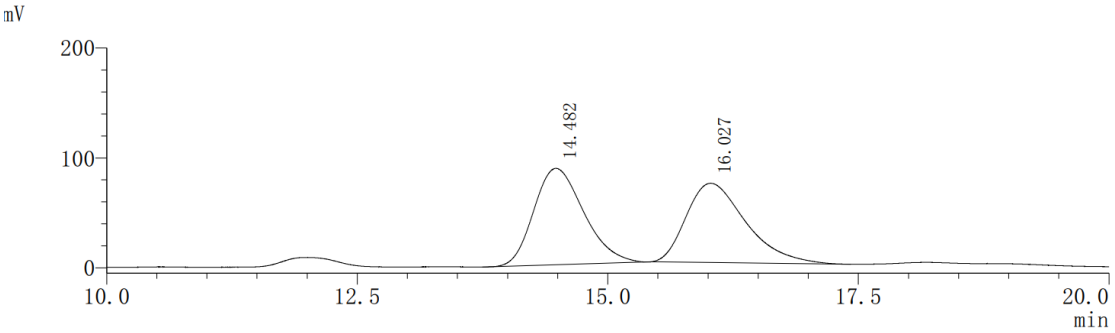
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.540	M	0.8720	2043142	62104	4.9743
2	26.918	M	1.0147	39031233	1002870	95.0257

In a nitrogen-filled glovebox, a flame-dried 10 mL Schlenk reaction tube equipped with a magnetic stir bar was charged with **7** (0.370 g, 0.8 mmol), diphenylphosphine (1.4 mL, 10.0 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 85 °C for 48 h. The mixture was concentrated under reduced pressure and purified by *via* column chromatography on silica gel (hexanes/Et_2O = 2:1) to afford 0.316 g product **8** in 61% yield with 91% ee (white solid). [**8**: 98% ee (after recrystallization)]. **^{1}H NMR (600 MHz, Chloroform-*d*)** δ 12.13 (s, 1H), 8.40 (s, 1H), 8.17 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.56 – 7.51 (m, 3H), 7.45 – 7.38 (m, 3H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.31 – 7.28 (m, 2H), 7.27 – 7.20 (m, 10H), 5.19 (s, 1H), 3.53 – 3.49 (m, 1H), 3.46 – 3.42 (m, 1H), 3.26 – 3.17 (m, 2H), 2.49 – 2.45 (m, 2H), 2.21 – 2.18 (m, 2H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 177.66, 167.78, 141.00 (d, *J* = 14.0 Hz), 140.91, 137.96, 137.52, 134.84, 133.46, 132.75 (d, *J* = 2.5 Hz), 132.63 (d, *J* = 2.3 Hz), 132.53, 130.33, 129.70 (d, *J* = 5.5 Hz), 128.74, 128.59 (d, *J* = 6.3 Hz), 128.55, 128.50, 128.45, 128.39, 128.35, 127.26, 126.66, 123.97, 52.24, 40.81, 40.41, 29.73 (d, *J* = 18.2 Hz), 29.23 (d, *J* = 12.5 Hz). **^{31}P NMR (243 MHz, Chloroform-*d*)** δ -14.95.

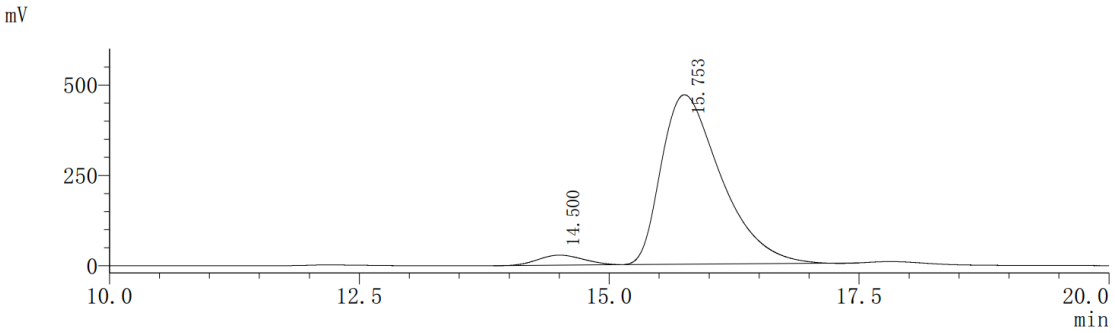
HRMS (ESI-TOF) (m/z): Calcd for $C_{37}H_{33}N_2NaOPS_3$, ($[M + Na]^+$), 671.1385; found 671.1333.

$[\alpha]_D^{19}$ = -6.3 (c = 1.0, CH_2Cl_2).

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 14.50 min, t_R (major) = 15.75 min, 91% ee.



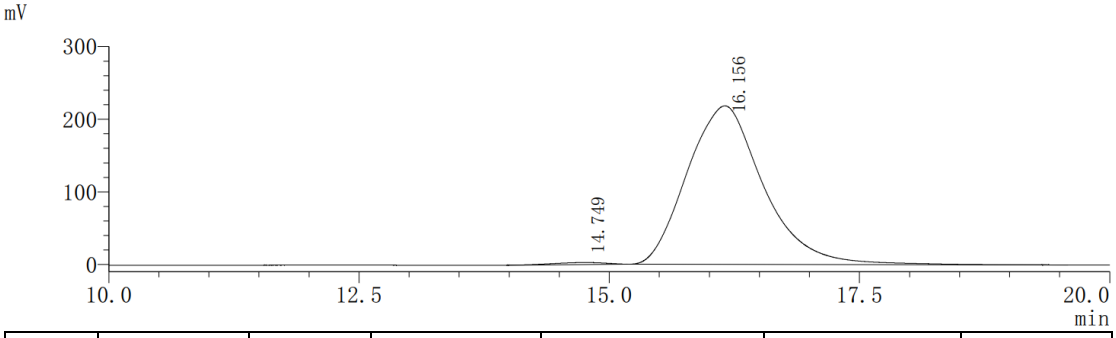
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	14.482	M	0.9180	3036369	87700	50.4791
2	16.027	M	1.0804	2978726	72121	49.5209



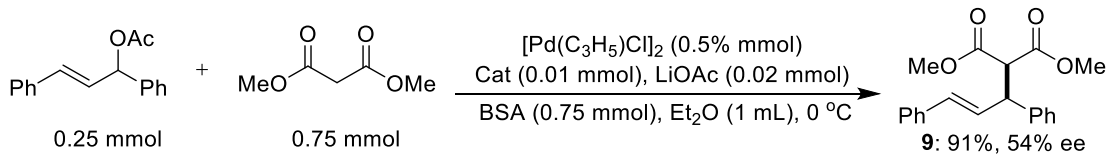
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	14.500	M	0.8451	875578	27774	4.3090
2	15.753	M	1.0921	19443933	468371	95.6910

HPLC of 8 after recrystallization

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 14.75 min, t_R (major) = 16.16 min, 98% ee.



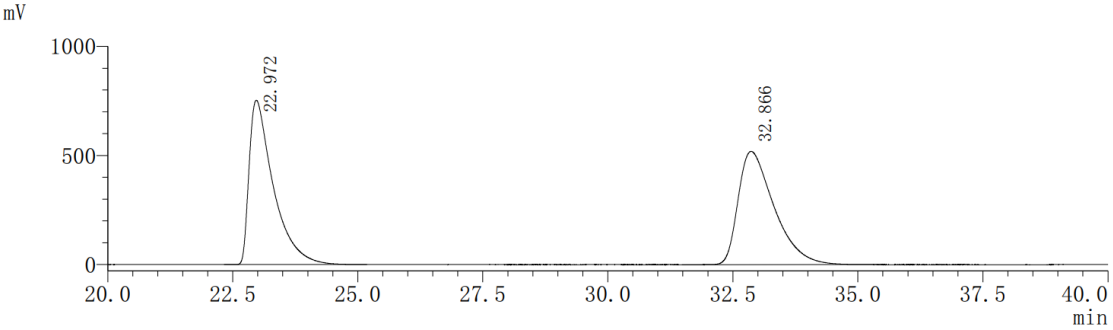
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	14.749	M	0.9051	99556	2778	0.8540
2	16.156	M	1.3967	11557565	218083	99.1460



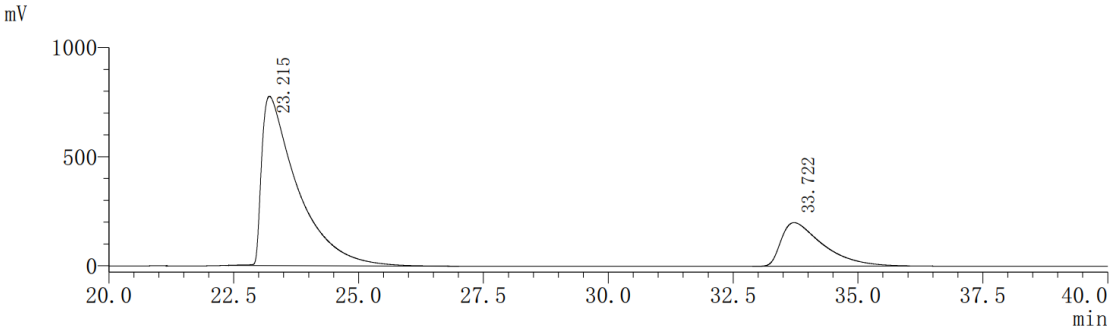
To a mixture of chiral ligand **8** (0.01 mmol), $[Pd(\eta\text{-}C_3H_5)Cl]_2$ (0.005 mmol, 1.4 mg) and LiOAc (0.02 mmol, 1.3 mg) in diethyl ether (1 mL) were added BSA (0.75 mmol, 152.0 mg) and allylic ester (0.25 mmol, 63.0 mg) at 0 °C under argon atmosphere. After 1 h, malonate (0.75 mmol) was added. After 36 h, the reaction mixture was diluted with diethyl ether and water. The organic layer was washed with brine and dried over Na_2SO_4. The filtrate was concentrated and purified by column chromatography to afford the product **9**. **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 7.33 – 7.18 (m, 10H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.33 (dd, *J* = 15.7, 8.6 Hz, 1H), 4.27 (dd, *J* = 10.9, 8.7 Hz, 1H), 3.95 (d, *J* = 10.9 Hz, 1H), 3.70 (s, 3H), 3.52 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 168.20, 167.79, 140.18, 136.84, 131.85, 129.13, 128.73, 128.49, 127.88, 127.58, 127.18, 126.40, 57.67, 52.64, 52.46, 49.21.

HRMS (ESI-TOF) (m/z): Calcd for $C_{20}H_{20}NaO_4$, ($[M + Na]^+$), 347.1254; found 347.1254.

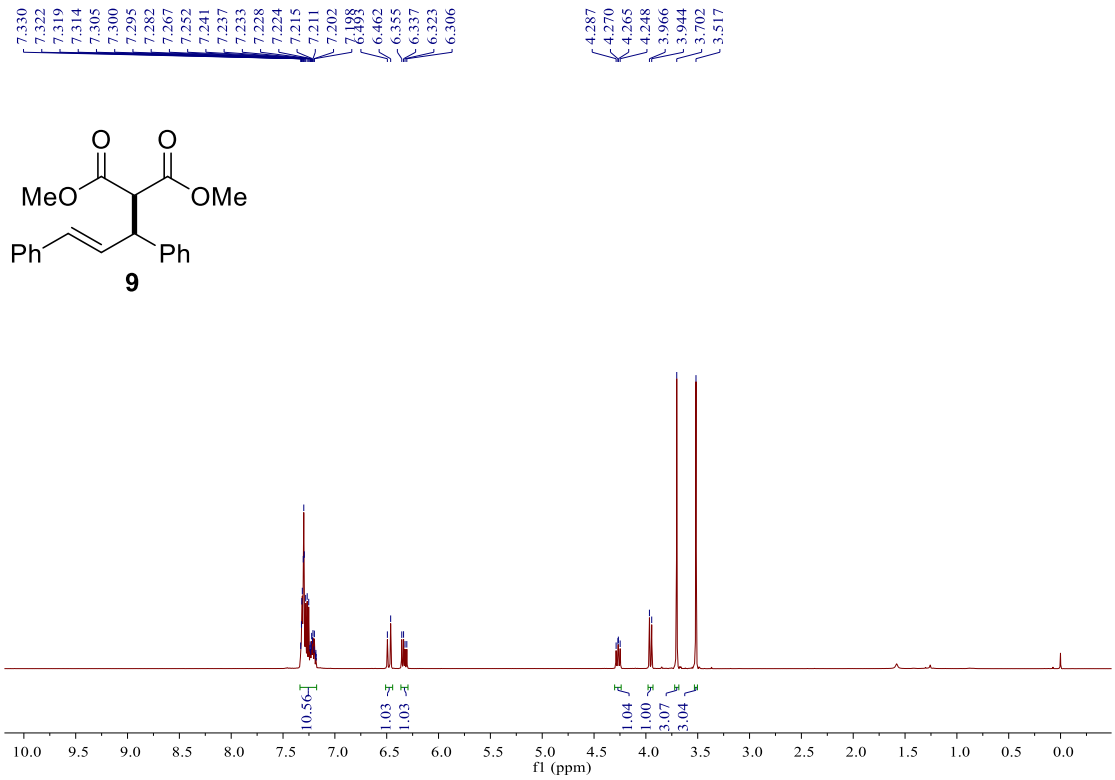
HPLC analysis: Daicel Chiralpak AD-3 column (97:3 hexane: 2-propanol, 1.0 mL/min, 25 °C, 254 nm); t_R (minor) = 23.22 min, t_R (major) = 33.72 min, 54% ee.



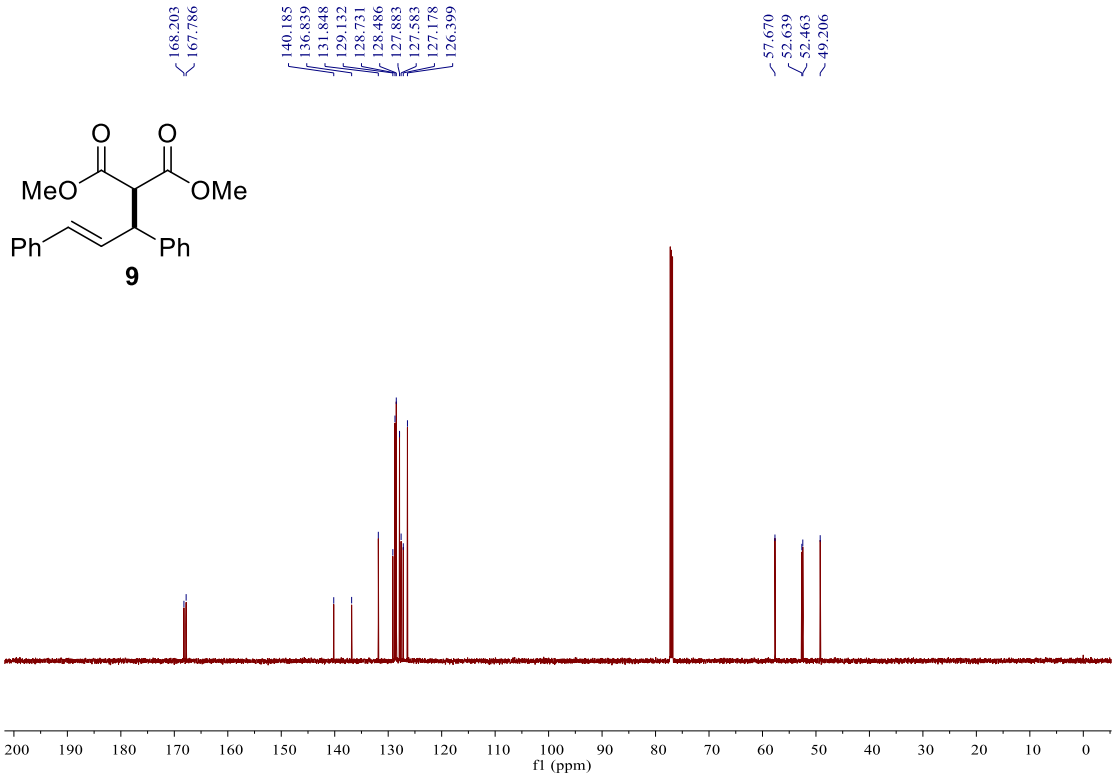
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	22.972	M	0.8412	25399486	754272	49.4491
2	32.866	M	1.3109	25965397	519655	50.5509



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	23.215	M	1.2638	38689255	776750	76.9770
2	33.722	M	1.5234	11571554	199754	23.0230



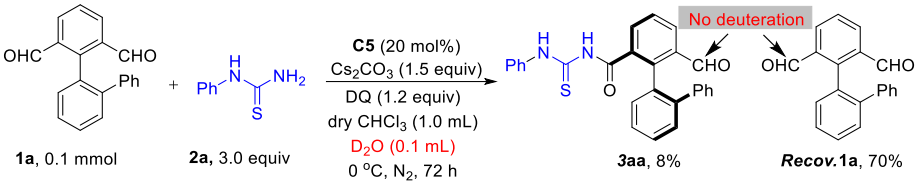
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 9.



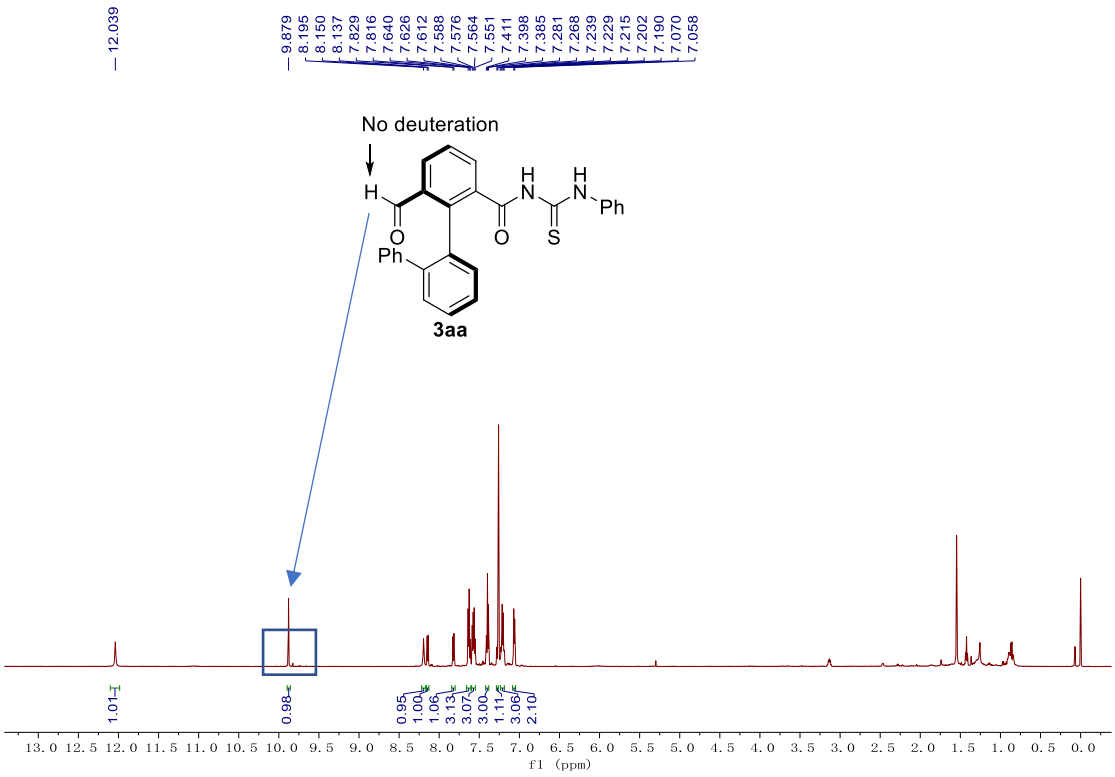
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 9.

IV. Mechanistic Studies

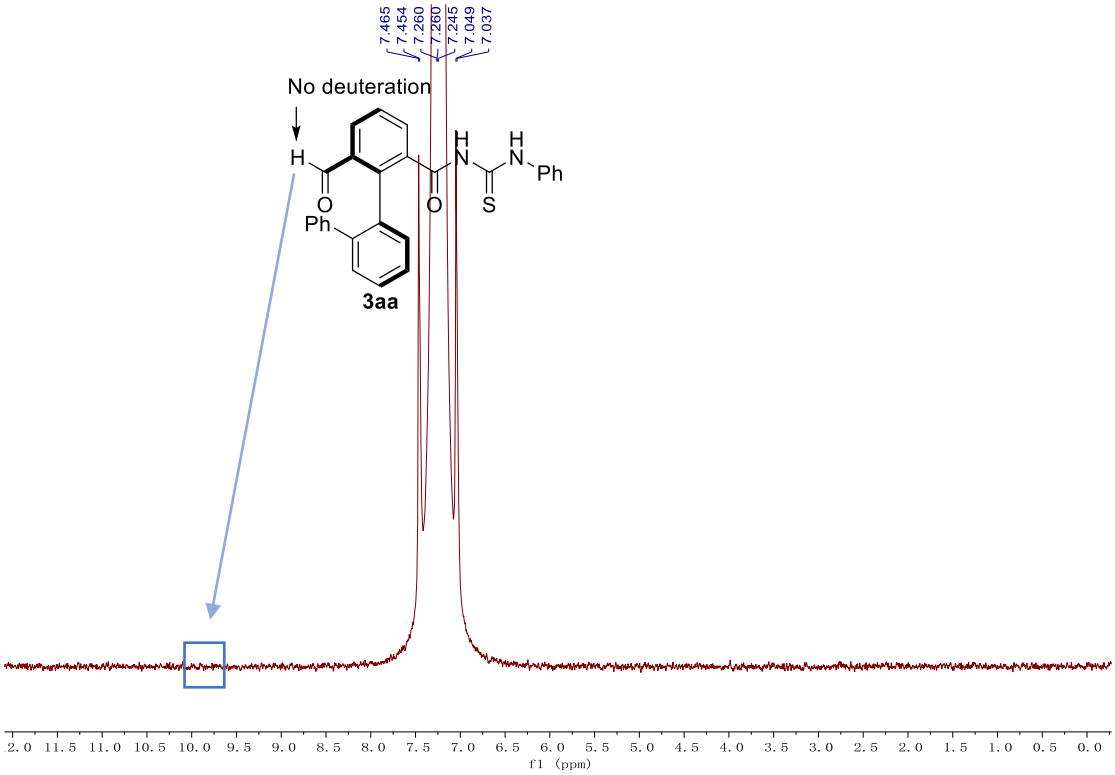
4.1 Deuterium labeling experiment



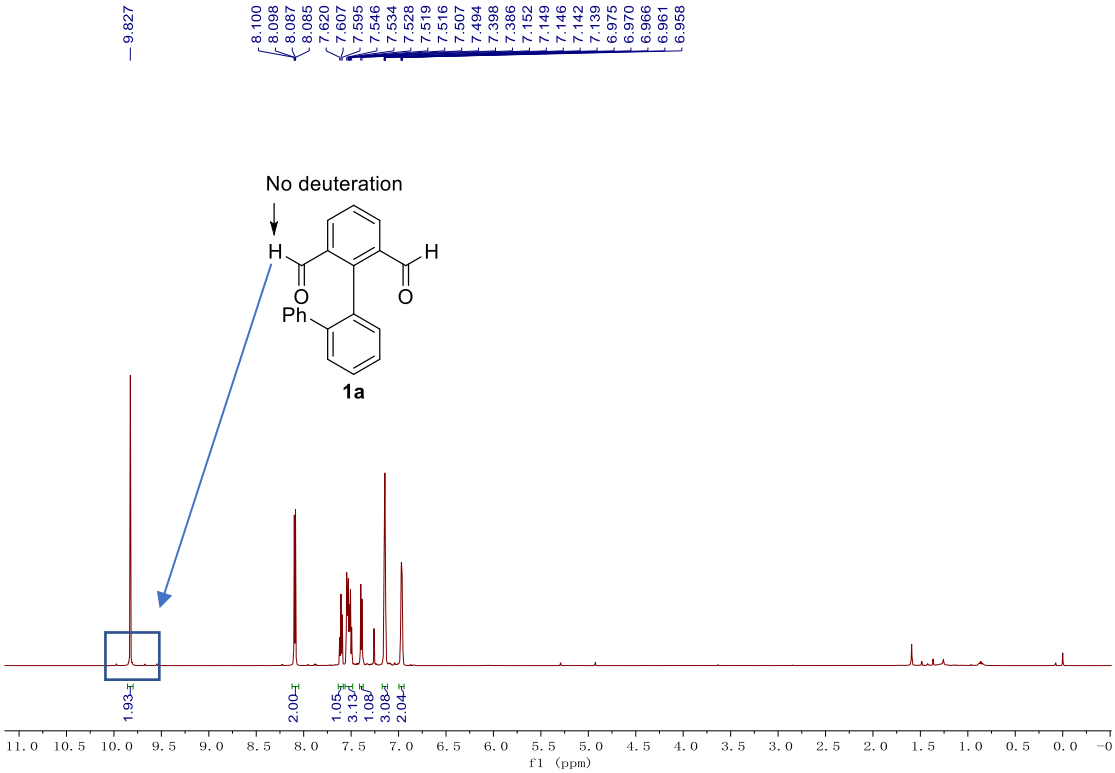
In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **C5** (20 mol%, 10.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), [1,1':2',1"-terphenyl]-2,6-dicarbaldehyde **1a** (0.1 mmol, 29 mg), anhydrous chloroform (1.0 mL), and D_2O (0.1 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **4a** (46.0 mg, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product *R*-**3aa**.



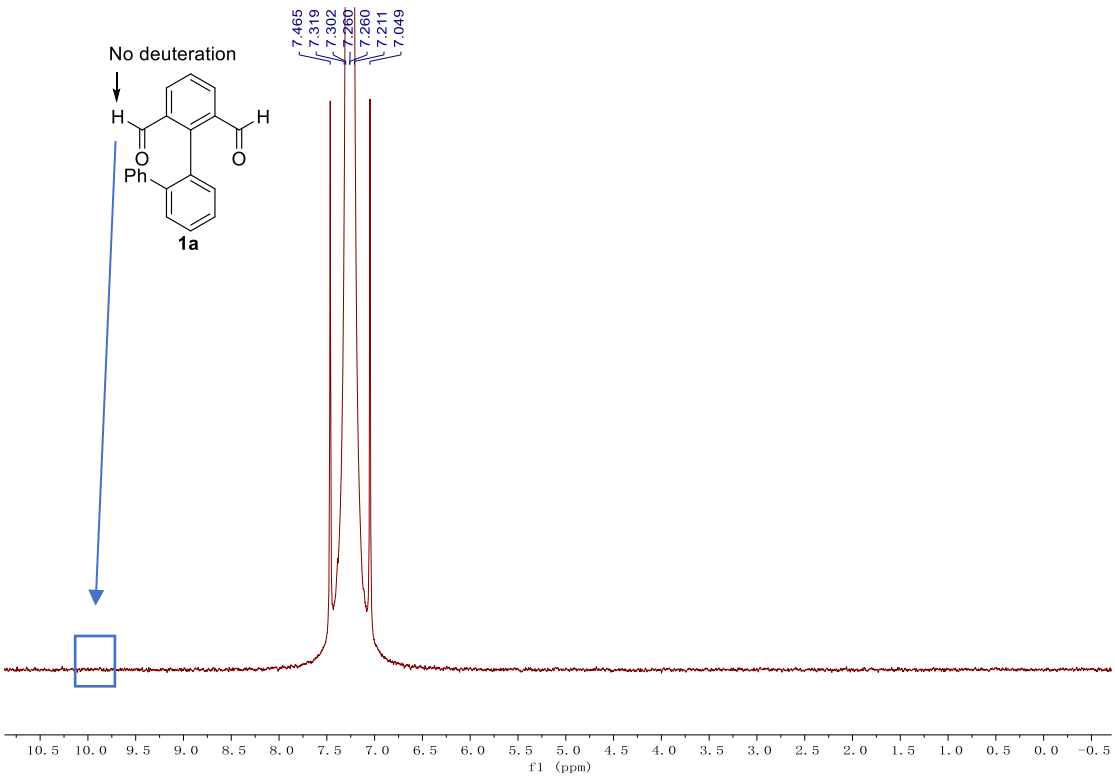
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3aa.



^{2}H NMR (77 MHz, $CDCl_3$) spectrum of 3aa.



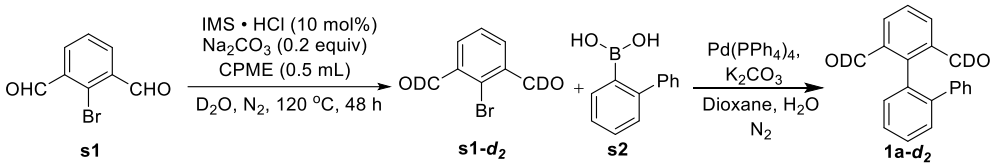
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of *Recov.* 1a.



^{2}H NMR (77 MHz, $CDCl_3$) spectrum of *Recov.* 1a.

4.2 Parallel Kinetic Isotope Effect Experiment

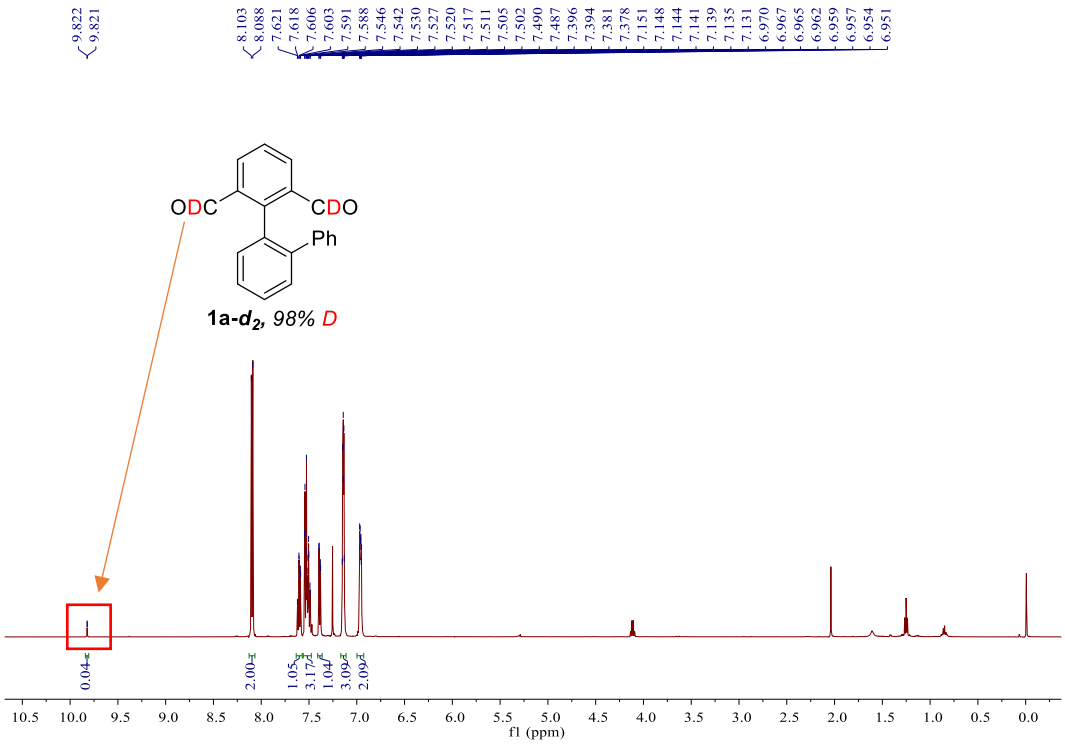
4.2.1 Procedure for synthesis of 1a-d_2[4]



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with aldehyde **s1** (0.5 mmol), IMes • HCl (17.0 mg, 0.05 mmol), Na_2CO_3 (11.0 mg, 0.1 mmol), CPME (0.5 mL) and D_2O (2.5 mL). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 120 ºC for 48 h, and extracted with AcOEt, and the organic layers were dried over MgSO4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (PE : EA = 10:1), **s1-*d*$_2$** was obtained in 90% yield, with 98% D.

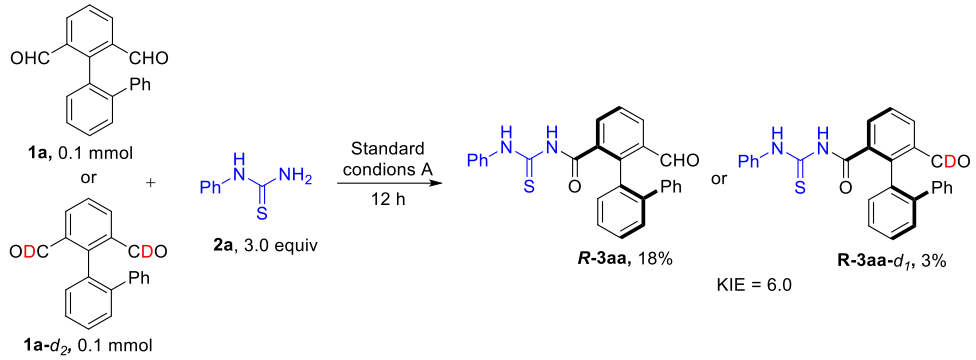
A flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with 2-bromoisophthalaldehyde **s1-*d*$_2$**, 2-biphenylboronic acid **s2** (2.29 equiv), K_2CO_3 (6.89 equiv) and $Pd(PPh_3)_4$ (0.018 equiv) and was evacuated and charged with argon three times. Then degassed 1,4-dioxane : water = 7 : 1 were added and the reaction was heated at 95 °C for 3 days under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate : cyclohexane = 1:20 to 1:10) and washed with ethanol to give compound as a white solid (yield: 75 %).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.82 (d, *J* = 0.8 Hz, 0.04 H), 8.10 (d, *J* = 7.7 Hz, 2H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.15 – 7.13 (m, 3H), 6.97 – 6.95 (m, 2H).

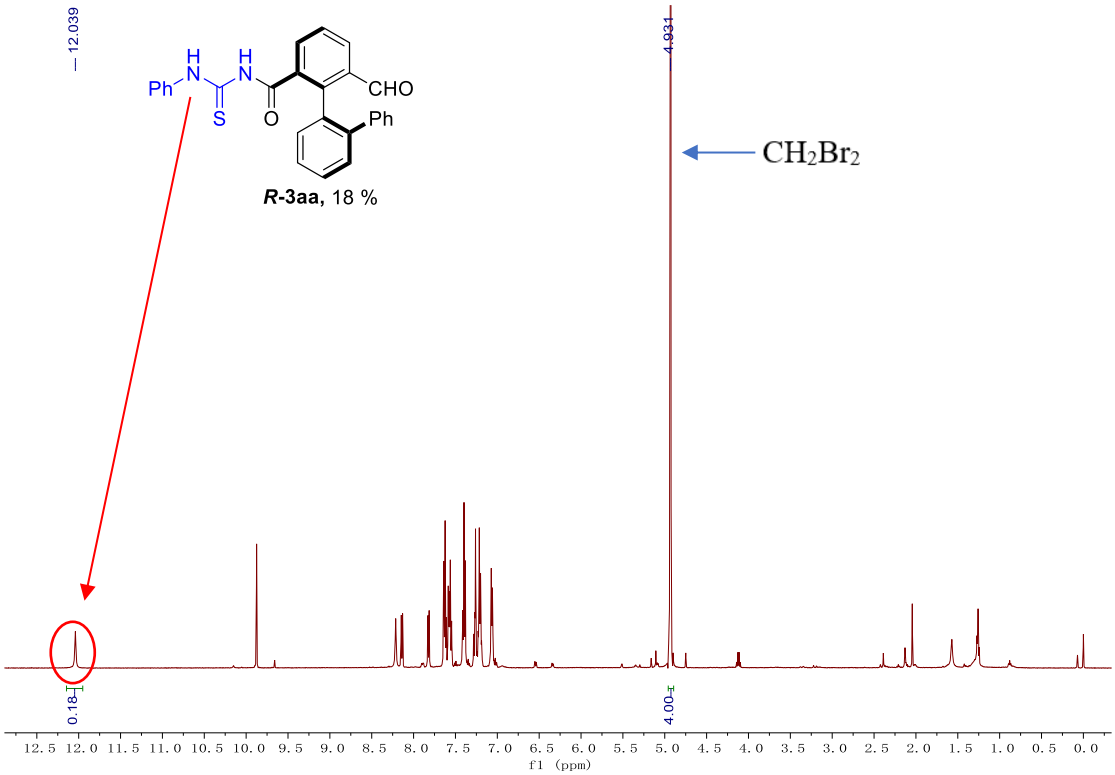


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1a-d_2.

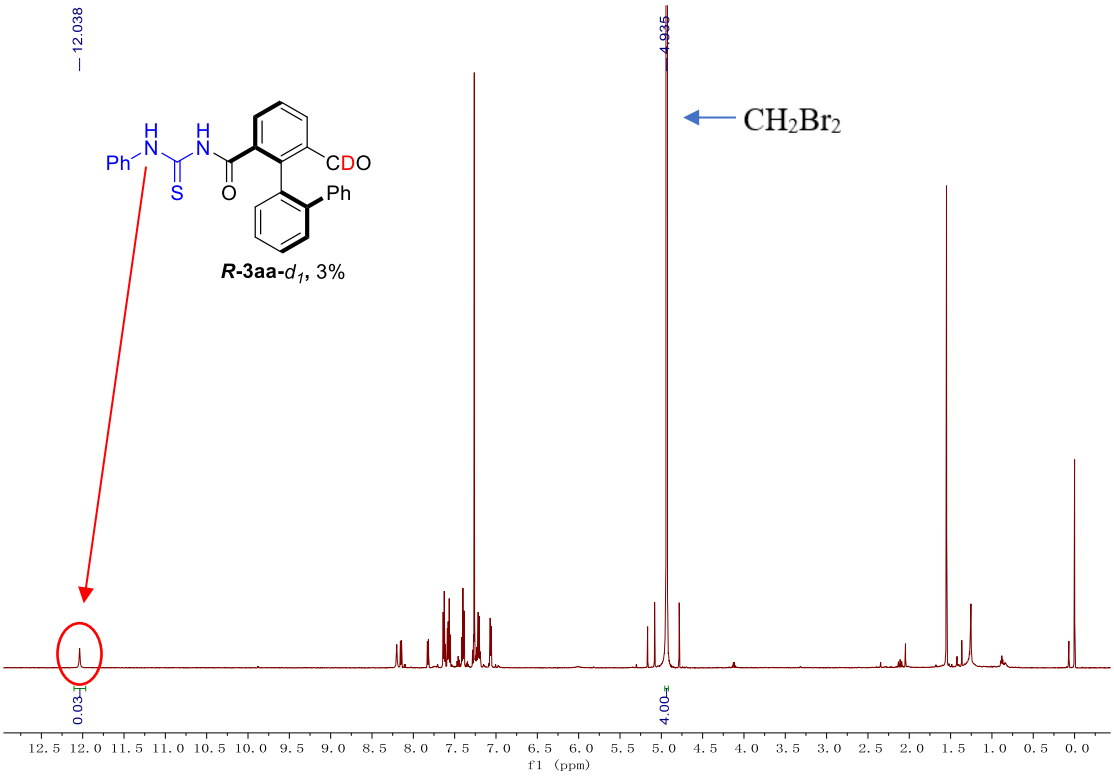
4.2.2 Experiment Procedure for the Isotope Experiments



In a nitrogen-filled glovebox, two flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **C5** (20 mol%, 10 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), **1a or 1a**-d_2 (0.1 mmol, 29.0 mg), and anhydrous chloroform (1.0 mL) was added. The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (46.0 mg, 3.0 equiv) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product ***R*-3aa**, yield: 18%; ***R*-3aa**-d_1, yield: 3%. The KIE was determined by ^{1}H NMR analysis to be 6.0.



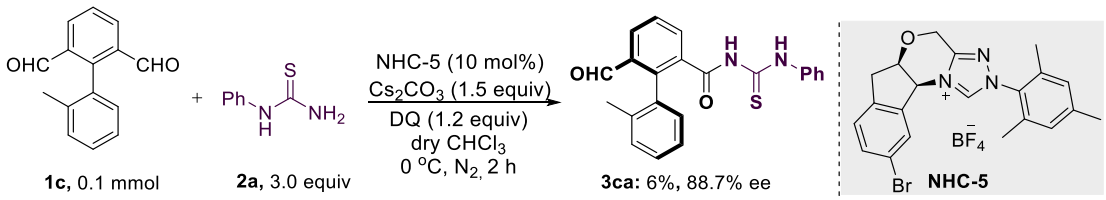
^{1}H NMR (600 MHz, $CDCl_3$) using CH_2Br_2 (0.2 mmol, 14.0 μL) as an internal standard of the reaction mixture (*R*-3aa)



^{1}H NMR (600 MHz, $CDCl_3$) using CH_2Br_2 (0.2 mmol, 14.0 μL) as an internal standard of the reaction mixture (*R*-3aa-d_1)

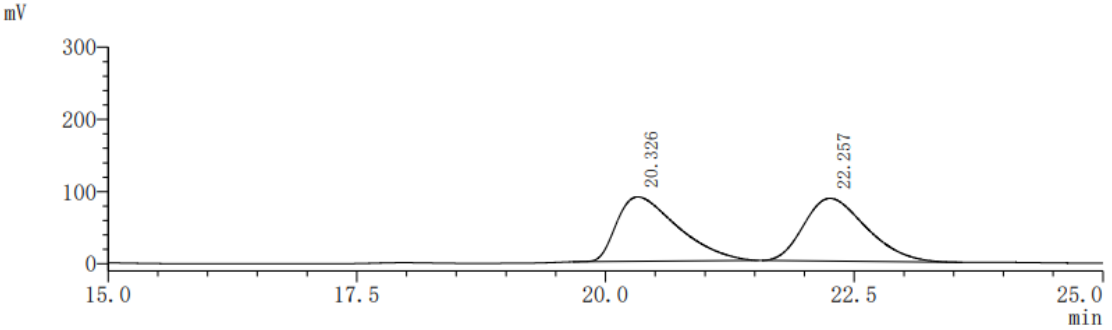
4.3 Control experiment

4.3.1 Investigation on the ee of the initial formed product 3ca

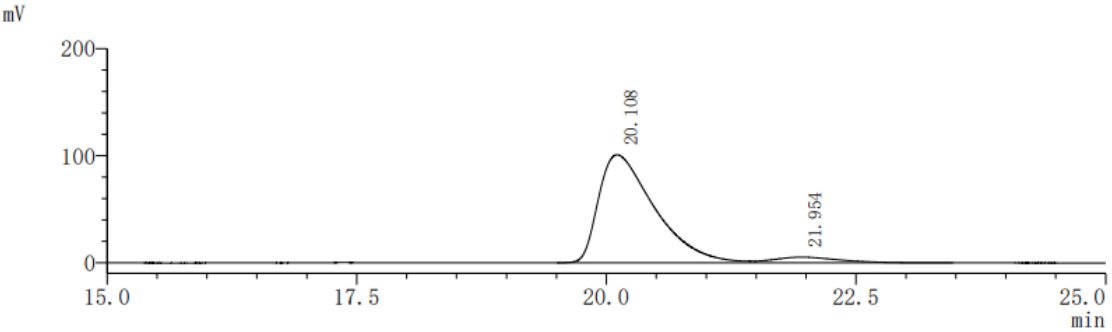


In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-5** (10 mol%, 5.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), 2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde **1c** (0.1 mmol, 22.4 mg) and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (46.0 mg, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 2 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product (*R*)-**3ca** (yield: 6%; 88.7% ee).

HPLC analysis: Daicel Chiralpak IC-3 column (95:5 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (major) = 20.11 min, t_R (minor) = 21.95 min, 88.7% ee.

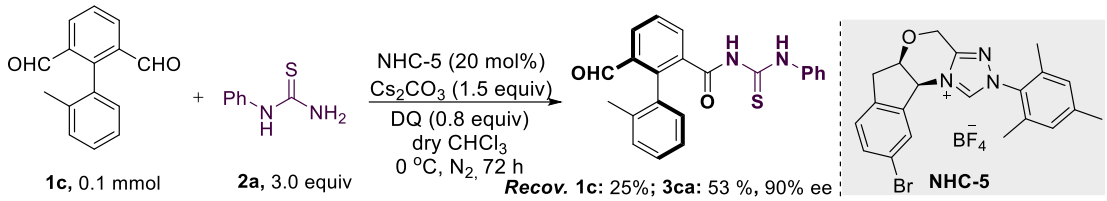


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.326	M	1.1502	3787902	89213	49.9556
2	22.257	M	1.1755	3794636	86859	50.0444



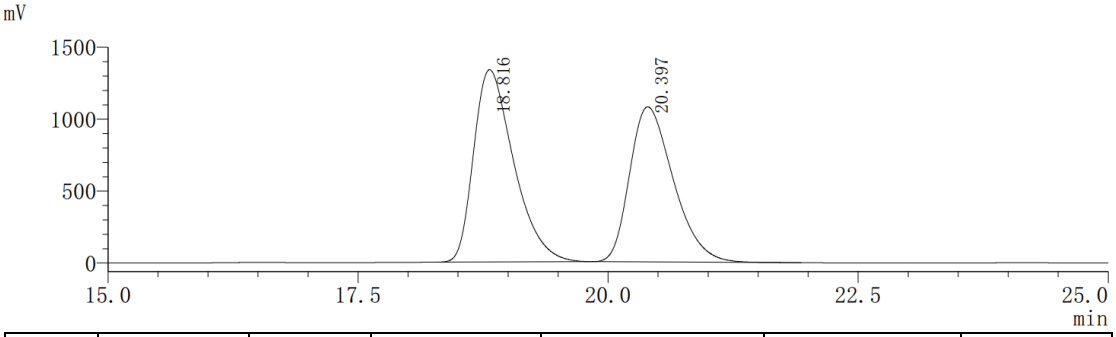
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.108	M	1.0243	3930111	100914	94.3524
2	21.954	M	1.2033	235242	5263	5.6476

4.3.2 Procedure for NHC-catalyzed Desymmetrization of Dialdehyde 1a with NHC-5.

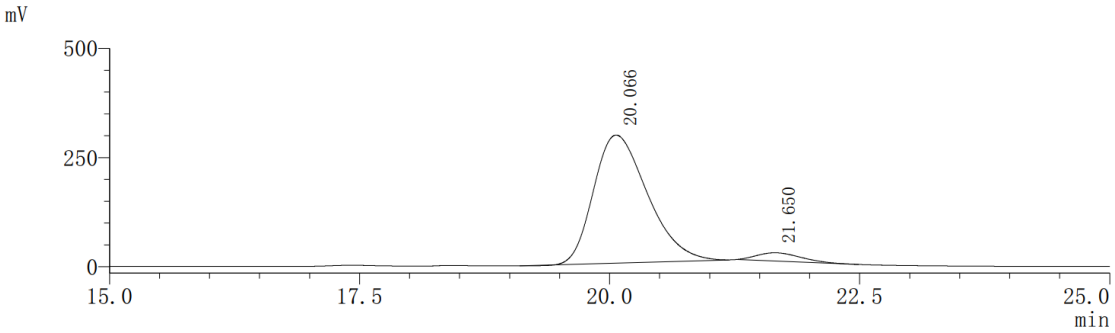


In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-5** (20 mol%, 10.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), 2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde **1c** (0.1 mmol, 22.4 mg) and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (46.0 mg, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (32 mg, 0.8 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 72 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product (*R*)**-3ca** (yield: 53%; 90% ee) and ***Recov.* 1c** (yield: 25%).

HPLC analysis: Daicel Chiralpak IC-3 column (95:5 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm); t_R (major) = 20.07 min, t_R (minor) = 21.65 min, 90% ee.

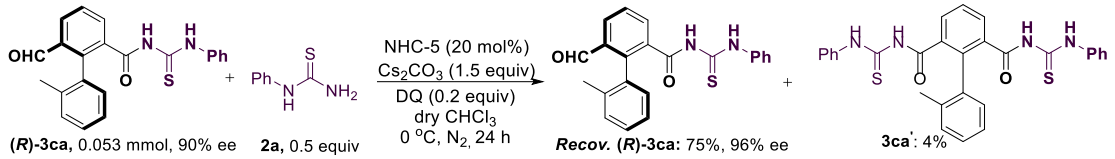


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.816	M	0.7265	37264452	1337010	53.2226
2	20.397	M	0.7983	32751813	1077898	46.7774



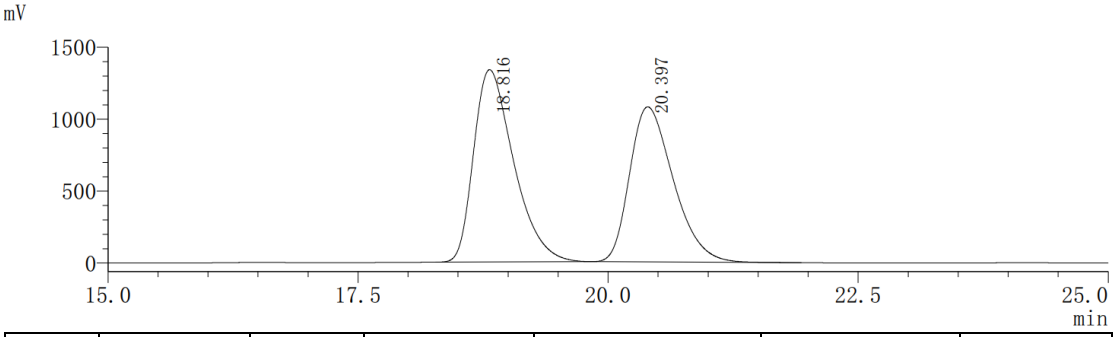
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.066	M	0.9942	10995182	293562	94.9061
2	21.650	M	0.8275	590144	19083	5.0939

4.3.3 General procedure for for NHC-catalyzed kinetic resolution (KR) of (*R*)-3ca with N-Phenylthiourea and characterization data.

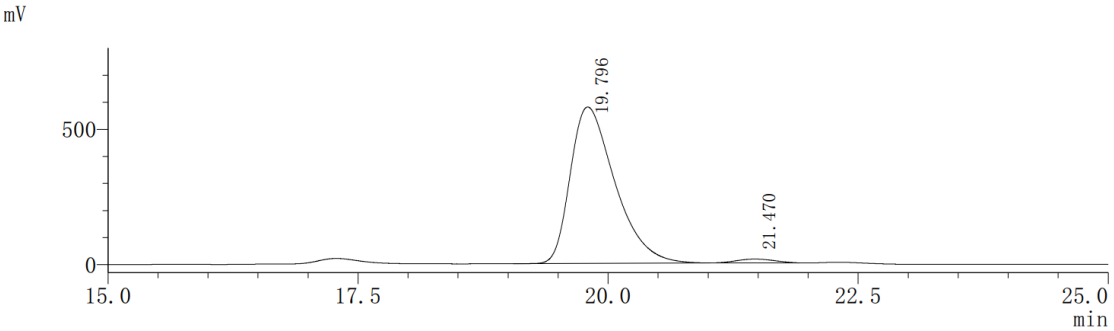


In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-5** (20 mol%, 5.3 mg), Cs_2CO_3 (26.0 mg, 1.5 equiv), (*R*)**-3ca** (0.053 mmol, 19.83 mg) and anhydrous chloroform (0.5 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (4.0 mg, 0.5 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (4.4 mg, 0.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ºC for 24 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product *Recov.* (*R*)**-3ca** (yield: 75%; 96% ee) and **3ca'** (yield: 4%).

HPLC analysis: Daicel Chiralpak IC-3 column (95:5 hexane: 2-propanol, 1 mL/min, 25 ºC, 254 nm); t_R (major) = 19.80 min, t_R (minor) = 21.47 min, 96% ee.

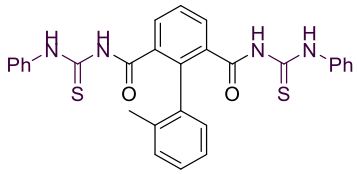


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	18.816	M	0.7265	37264452	1337010	53.2226
2	20.397	M	0.7983	32751813	1077898	46.7774

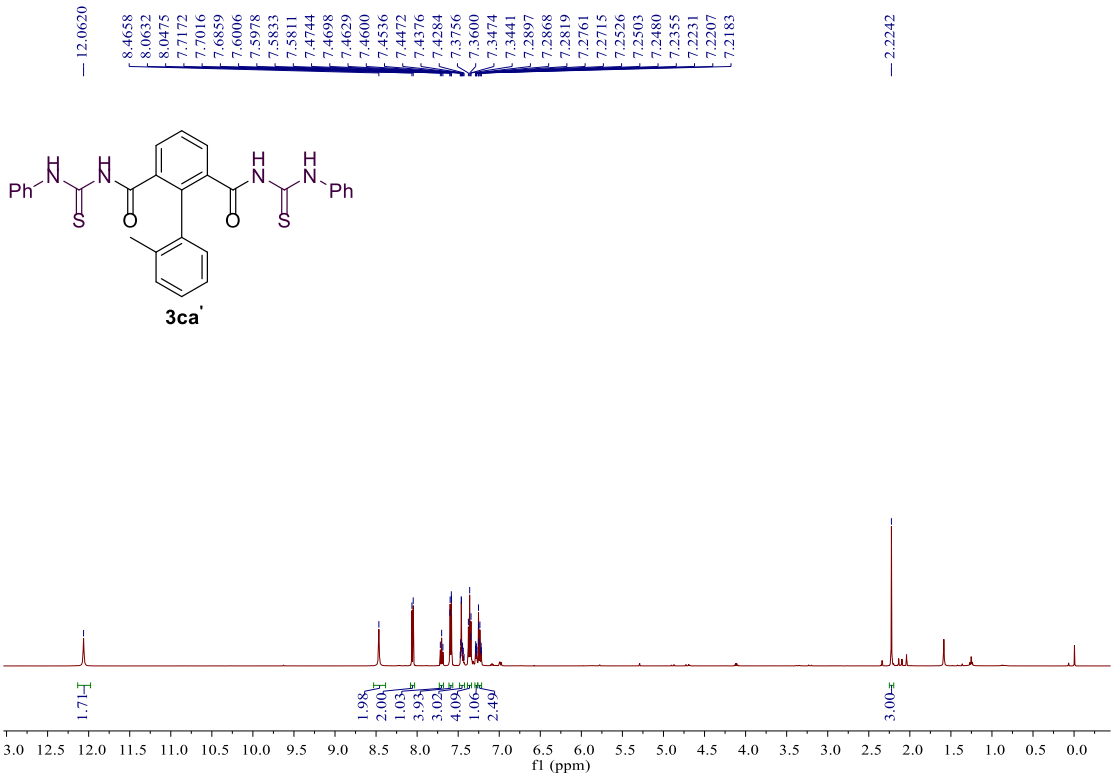


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.796	M	0.8118	17946422	578014	98.0405
2	21.470	M	0.7045	358681	13954	1.9595

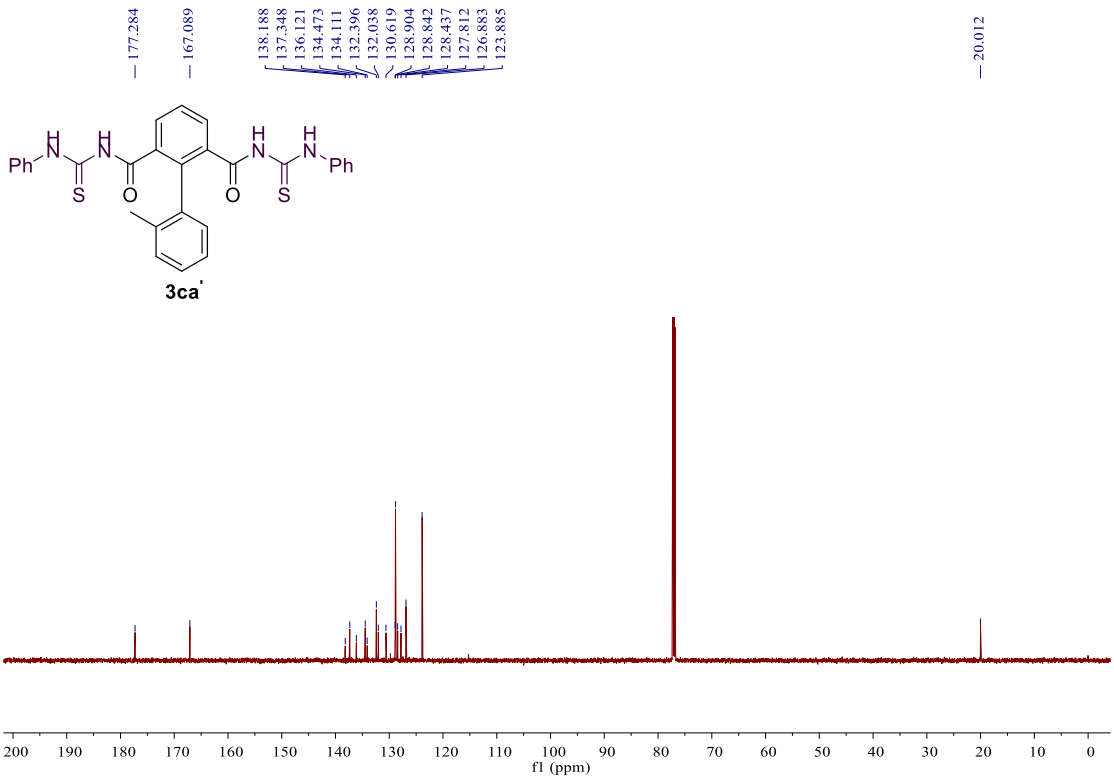
2'-methyl-*N*^{2}, *N*^{6}-bis(phenylcarbamothioyl)-[1,1'-biphenyl]-2,6-dicarboxamide 3ca'



3ca': **^{1}H NMR (500 MHz, Chloroform-*d*)** δ 12.06 (s, 2H), 8.47 (s, 2H), 8.06 (d, J = 7.9 Hz, 2H), 7.70 (t, J = 7.8 Hz, 1H), 7.61 – 7.58 (m, 4H), 7.47 – 7.43 (m, 3H), 7.38 – 7.34 (m, 4H), 7.29 – 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 2.22 (s, 3H). **^{13}C NMR (150 MHz, Chloroform-*d*)** δ 177.28, 167.09, 138.19, 137.35, 136.12, 134.47, 134.11, 132.40, 132.04, 130.62, 128.90, 128.84, 128.44, 127.81, 126.88, 123.89, 20.01. **HRMS** (ESI-TOF) (m/z): Calcd for $C_{29}H_{24}N_4NaO_2S_2$, ([M + Na]$^+$), 547.1233; found 547.1232.

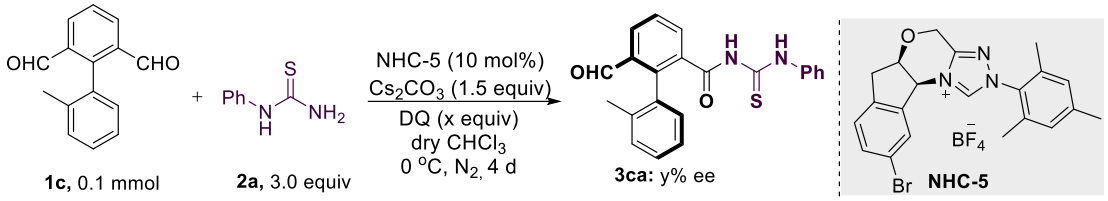


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ca'



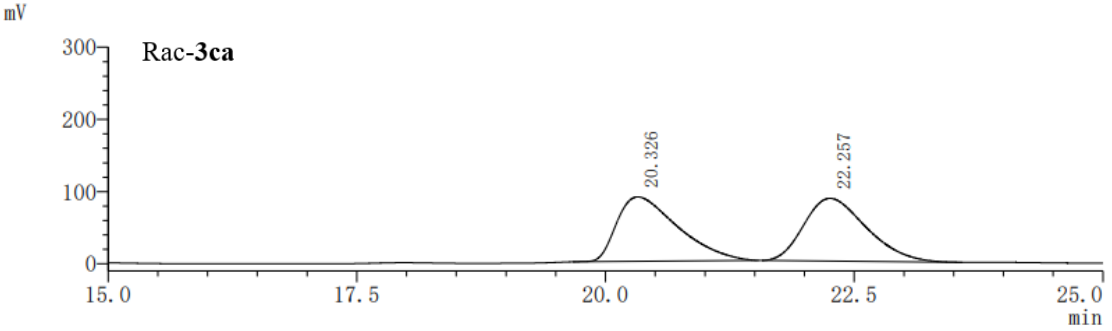
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ca'

4.3.4 Investigation on ee of the product 3ca by changing the amount of DQ

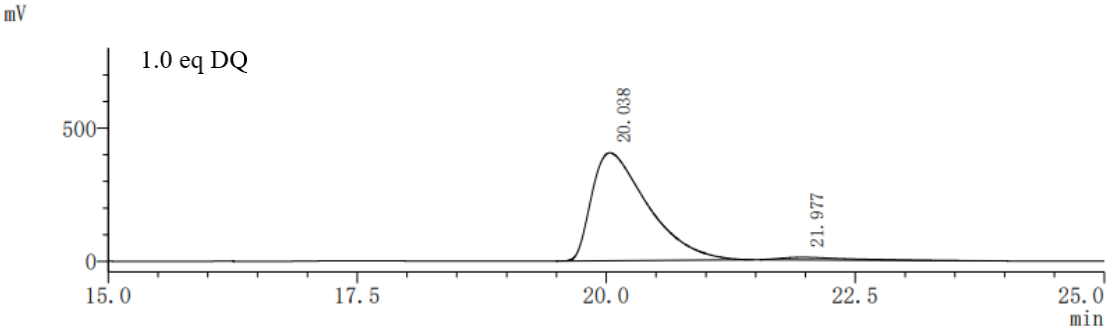


In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged **NHC-5** (10 mol%, 5.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), 2'-methyl-[1,1'-biphenyl]-2,6-dicarbaldehyde **1c** (0.1 mmol, 22.4 mg) and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (46.0 mg, 3.0 equiv) and 3,3´,5,5´-tetra-*tert*-butyldiphenoquinone (x equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 °C for 4 d. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product (*R*)-**3ca** (y% ee).

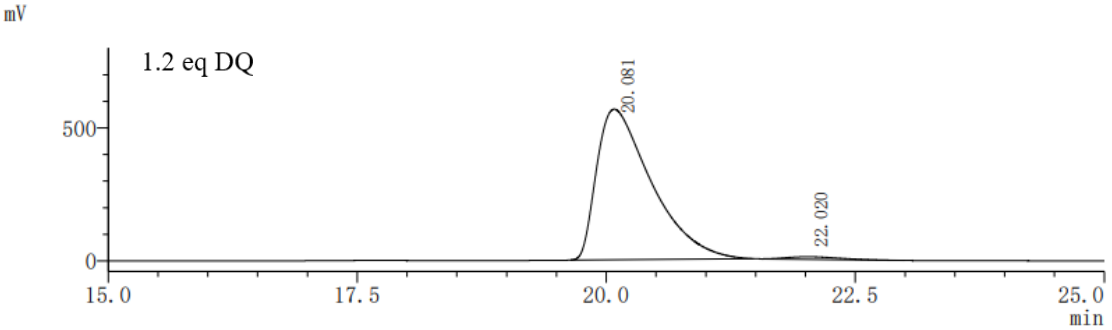
HPLC analysis: Daicel Chiralpak IC-3 column (95:5 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm).



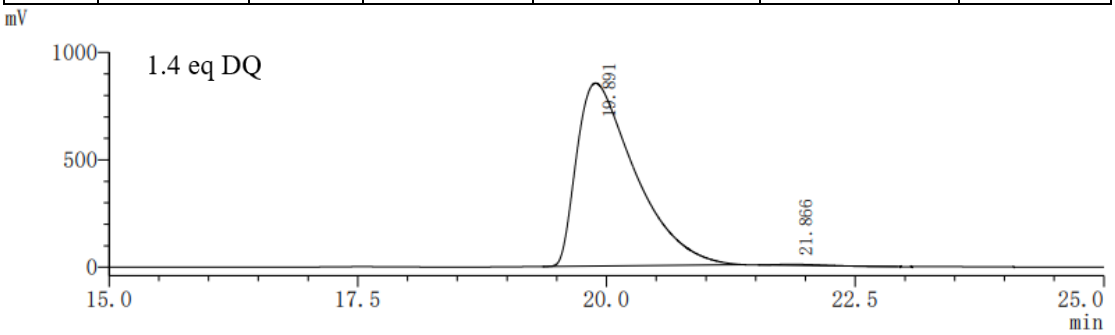
Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.326	M	1.1502	3787902	89213	49.9556
2	22.257	M	1.1755	3794636	86859	50.0444



Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.038	M	1.0350	15813470	404624	97.1246
2	21.977	M	1.1853	468167	9785	2.8754

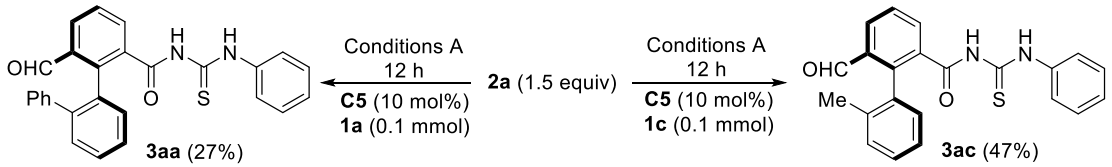


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	20.081	M	1.0037	21684615	566091	98.3659
2	22.020	M	1.0016	360236	9796	1.6341

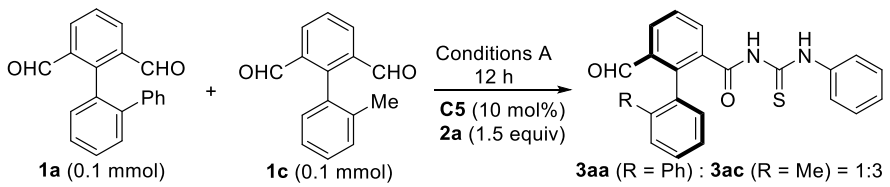


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	19.891	M	1.0734	34862555	851633	99.5716
2	21.866	M	0.8383	150002	4993	0.4284

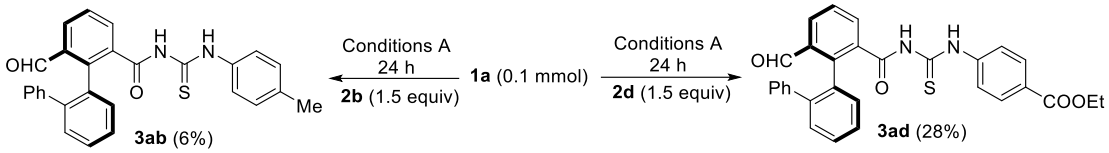
4.4 Competing experiment



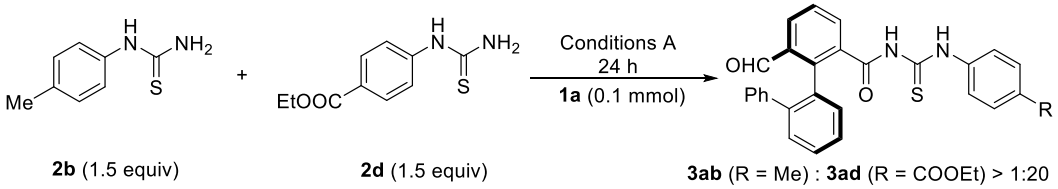
In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **C5** (10 mol%, 5.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), **1a** (0.1 mmol, 29 mg) or **1c** (0.1 mmol, 22.4 mg), and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (23.0 mg, 1.5 equiv) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product **3aa** (yield: 27%); **3ac** (yield: 47%).



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **C5** (10 mol%, 5.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), **1a** (0.1 mmol, 29 mg), **1c** (0.1 mmol, 22.4 mg), and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of N-Phenylthiourea **2a** (23.0 mg, 1.5 equiv) and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product **3aa** (yield: 11%); **3ac** (yield: 34%).



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **C5** (20 mol%, 10.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), **1a** (0.1 mmol, 29 mg), and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of 1-(p-tolyl)thiourea **2b** (25.0 mg, 1.5 equiv) or ethyl 4-thioureidobenzoate **2d** (34.0 mg, 1.5 equiv), and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 24 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product **3ab** (yield: 6%); **3ad** (yield: 28%).



In a nitrogen-filled glovebox, a flame-dried screw-cap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with **C5** (20 mol%, 10.0 mg), Cs_2CO_3 (49.0 mg, 1.5 equiv), **1a** (0.1 mmol, 29 mg), and anhydrous chloroform (1.0 mL). The mixture was stirred for 5 minutes, followed by the addition of 1-(p-tolyl)thiourea **2b** (25.0 mg, 1.5 equiv), ethyl 4-thioureidobenzoate **2d** (34.0 mg, 1.5 equiv), and 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone (48 mg, 1.2 equiv). Then the tube was sealed with a Thermo Scientific PTFE screw cap equipped with a septum, removed from the glovebox. The reaction mixture was stirred at 0 ℃ for 24 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate 10:3 (v/v) to give the product **3ab** (n.d.); **3ad** (yield: 29%).

V Determination of Rotational Barrier and half-life for C-C Bond.[5]

Following the procedure of Curran,[5c] compound **3aa** (5 mg) was dissolved in toluene (5 mL) to make a 1 mg/mL solution in a sealed tube. The tube was kept in a pre-equilibrated metal bath maintained at 90 °C. At 60 min time intervals, the sealed tube was taken out briefly (1-2 min) from the metal bath and a 70 μL aliquot was diluted with ^{i}PrOH (0.5 mL) taken out via syringe and injected onto the analytical HPLC column to determine the er. This er was plotted against time, and the barrier to rotation was calculated from the plot. In the y-axis of the graph, "m" stands for the % of the minor enantiomer, and "M" denotes the % of the major enantiomer. All the data have been recorded at 363.15 K (90 °C). The rate value can be inserted into **Equation 2** to give $\Delta G^{\ddagger}_{363.15\ K}$ and into **Equation 1** to give the half-life to racemisation.

k_B = Boltzmann's constant [1.381 x 10^{-23}J K^{-1}],

T = temperature in K,

h = Planck's constant [6.626 x 10^{-34} J s],

R = gas constant [8.3145 J mol^{-1}].

Then the simplified equation for racemization is:

$$\ln [(M + m) / (M - m)] = k_{rac}t + c = 2k_{rot}t + c$$

$$k_{rot} = (\text{slope}/2)$$

$$t_{½rac} = \ln(2)/k_{rac} \quad \textbf{Equation 1}$$

The experimental data is shown for 3aa below:

Time (min)	% of major enantiomer (M)	% of minor enantiomer (m)	M + m	M - m	(M + m) / (M - m)	ln [(M + m) / (M - m)]
0	98.2154	1.7846	100	96.4308	1.03701	0.036342
60	97.0695	2.9305	100	94.1390	1.06226	0.060399
120	95.9186	4.0814	100	91.8372	1.08888	0.085150
180	94.8148	5.1852	100	89.6296	1.11570	0.109482
240	93.6251	6.3749	100	87.2502	1.14613	0.136391
300	92.6179	7.3821	100	85.2358	1.17322	0.159752
360	91.5662	8.4338	100	83.1324	1.20290	0.184735
420	90.6864	9.3136	100	81.3728	1.22891	0.206128
480	89.5789	10.4211	100	79.1578	1.26330	0.233727
540	88.2218	11.7782	100	76.4436	1.30815	0.268614
600	87.2411	12.7589	100	74.4822	1.34260	0.294608
660	86.2777	13.7223	100	72.5554	1.37826	0.320822
720	85.1850	14.8150	100	70.3700	1.42106	0.351403
780	84.1910	15.8090	100	68.3820	1.46237	0.380058
840	83.3540	16.6460	100	66.7080	1.49907	0.404845

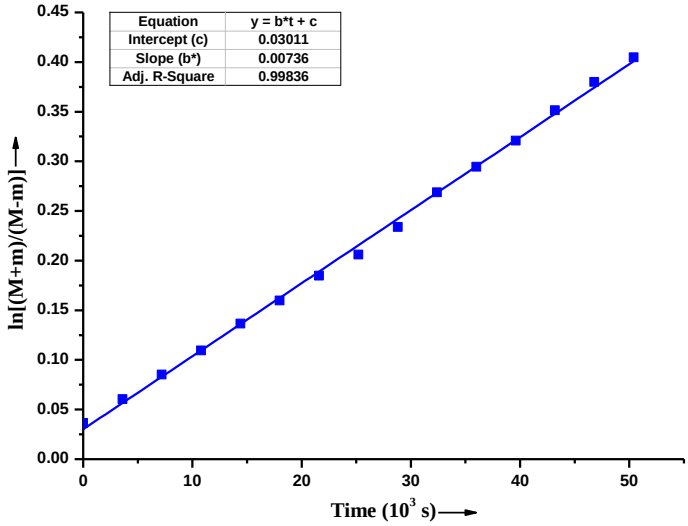


Figure S2. *Plot for the Determination of Rotational Barrier and Half-Life for C-C Bond in* ***3aa***.

So, from plot, $k_{rot} = [(0.00736 \times 10^{-3})/2] = 3.68 \times 10^{-6}\ s^{-1}$

$k^{\ddagger}_{rot} = [\ (k_{rot} \times h)/k_B T\ ] = 0.486 \times 10^{-18}$

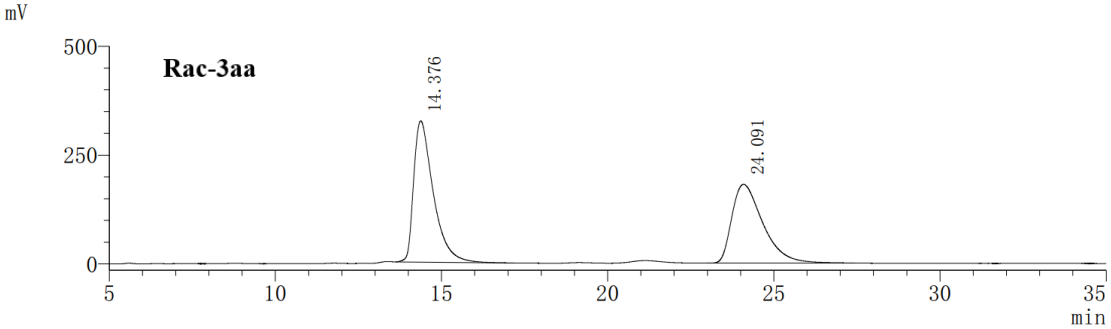
$\Delta G^{\ddagger}_{rot} = -RTlnk^{\ddagger}_{rot}$ **Equation 2**

= 127.323 kJ/mol = 30.4 kcal/mol

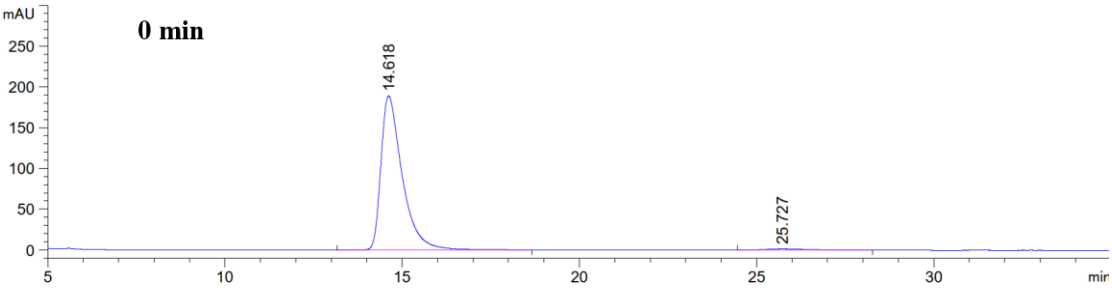
$t_{½rac} = \ln(2)/k_{rac} = 26.16$ h

HPLC data for the Analysis of C-C Bond Rotational Barrier:

HPLC analysis: Daicel Chiralpak OD-3 column (95:5 hexane: 2-propanol, 1 mL/min, 25 °C, 254 nm)

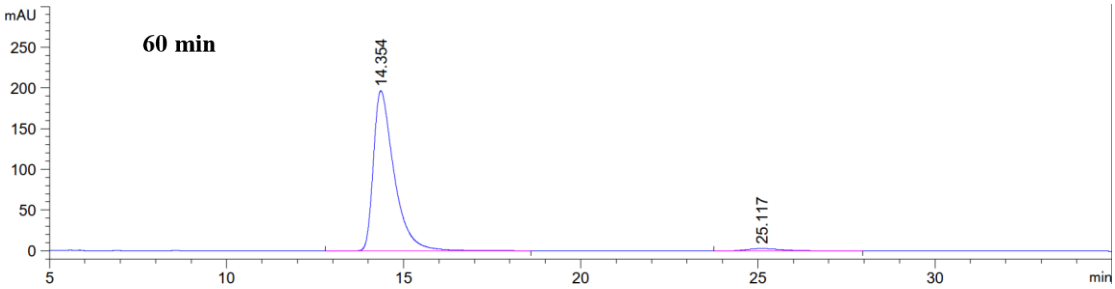


Peak	PetTime	Type	Width(min)	Area	Hight	Area%
1	14.376	M	1.0422	13350854	325016	53.1707
2	24.091	M	1.6871	11758587	181154	46.8293

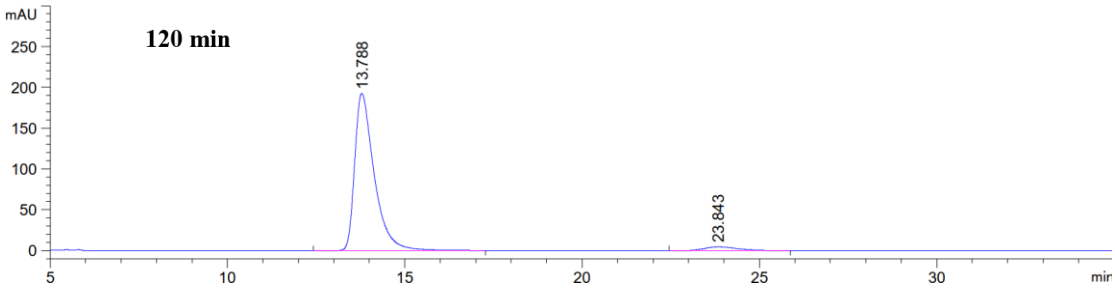


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.618	BB	0.6242	7912.22314	189.06305	98.2154

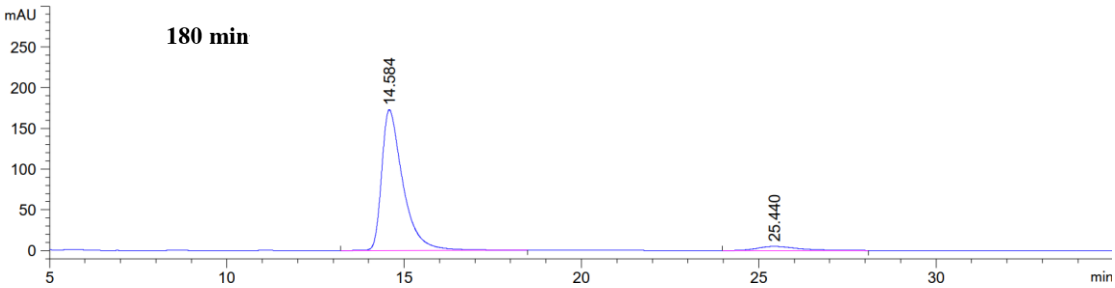
2	25.727	BB	0.9687	143.76436	1.74594	1.7846



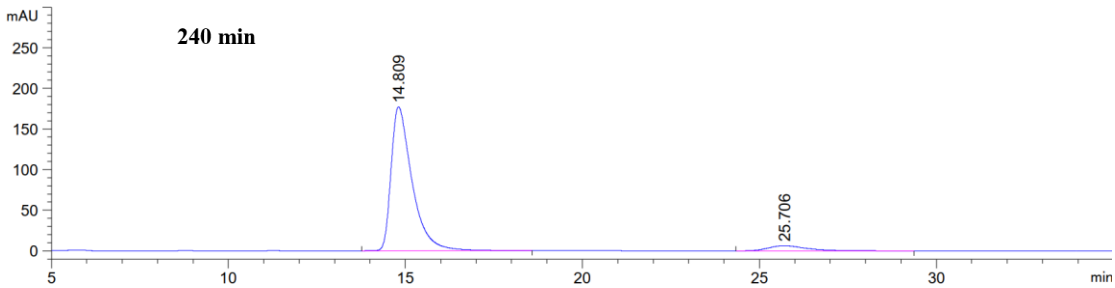
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.354	BB	0.6055	8040.97168	196.85754	97.0695
2	25.117	BB	1.0361	242.75339	3.04498	2.9305



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	13.788	BB	0.5697	7385.20410	192.86766	95.9186
2	23.843	BB	0.9357	314.24542	4.66026	4.0814

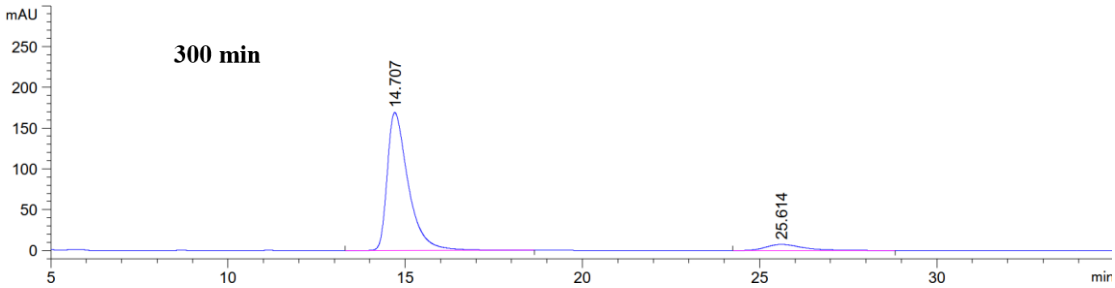


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.584	BB	0.6142	7170.65723	172.77100	94.8148
2	25.440	BB	0.9646	392.14893	5.00757	5.1852

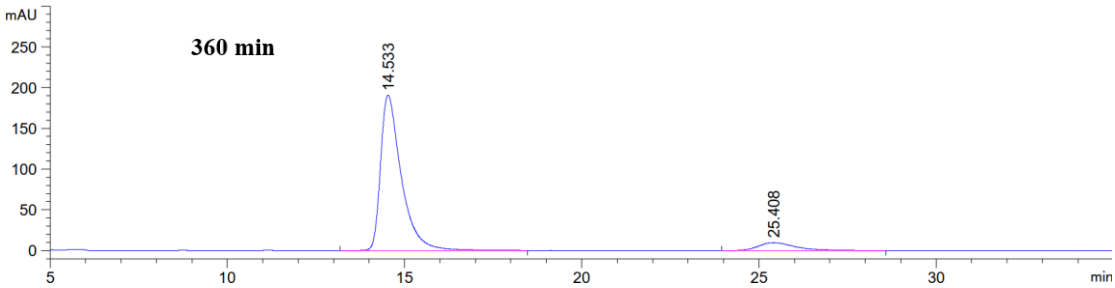


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.809	BB	0.6154	7309.73096	177.13809	93.6251

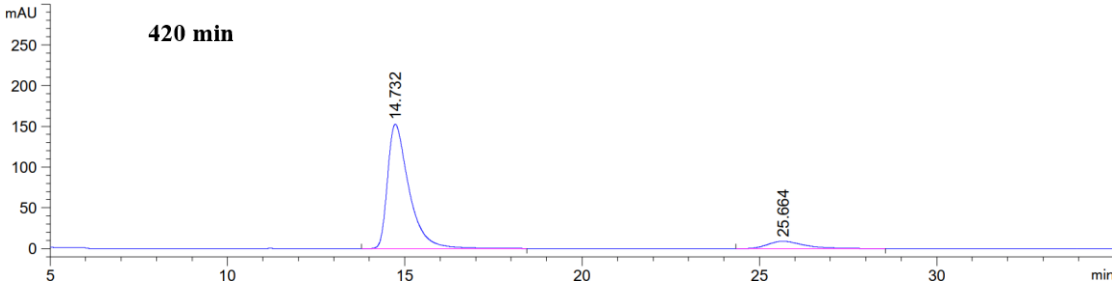
2	25.706	BB	1.0469	497.71701	6.45283	6.3749



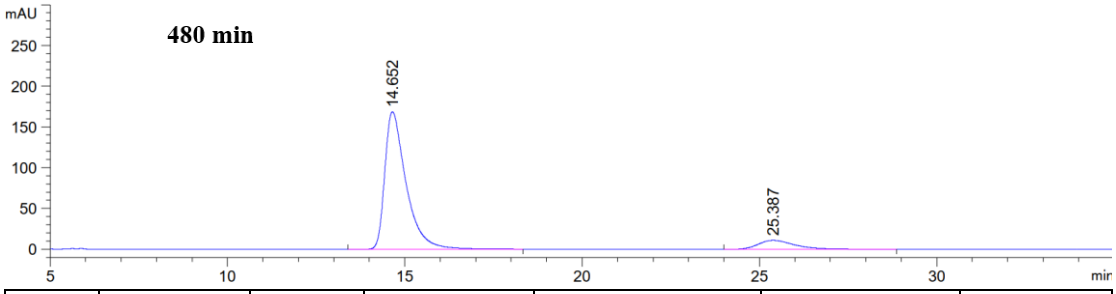
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.707	BB	0.6210	6991.26270	169.23021	92.6179
2	25.614	BB	1.0437	557.23962	7.58856	7.3821



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.533	BB	0.6048	7756.63428	191.00586	91.5662
2	25.408	BB	1.0515	714.43402	9.73142	8.4338

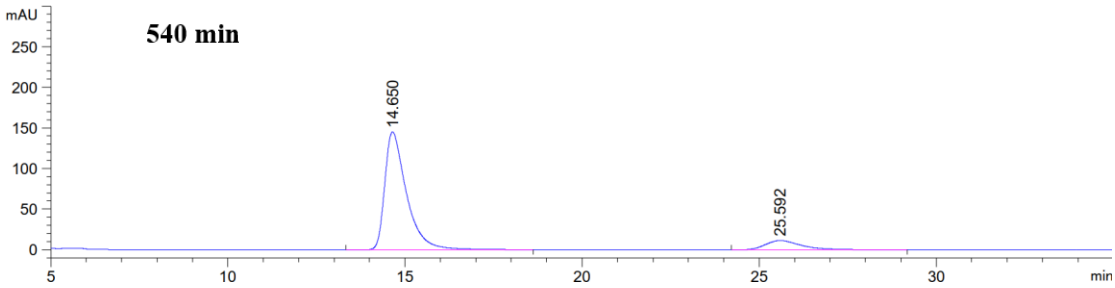


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.732	BB	0.6259	6417.58740	152.84164	90.6864
2	25.664	BB	1.0275	659.09027	8.96764	9.3136

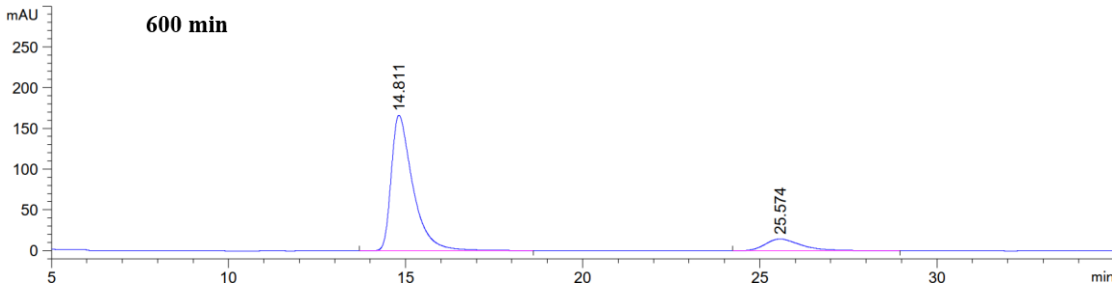


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.652	BB	0.6197	7060.84717	168.90300	89.5789

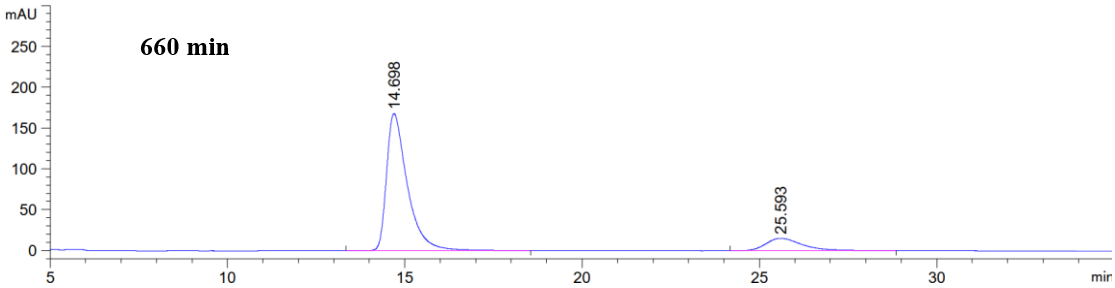
2	25.387	BB	1.0511	821.42194	11.14206	10.4211



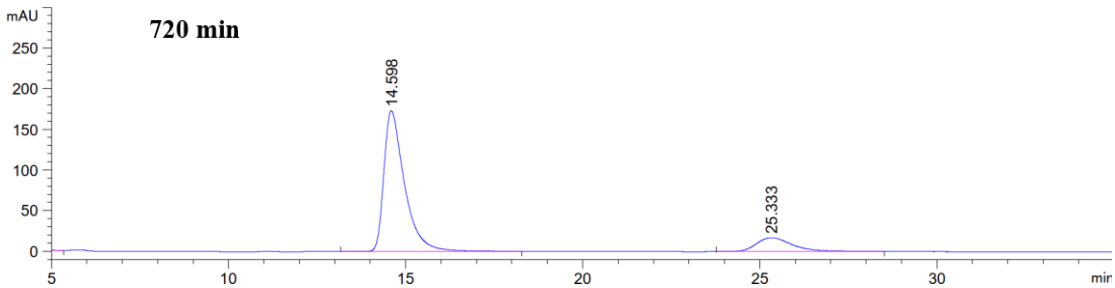
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.650	BB	0.6318	6214.73340	145.35599	88.2218
2	25.592	BB	1.0148	829.70807	11.47188	11.7782



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.811	BB	0.6294	7061.96240	166.29501	87.2411
2	25.574	BB	1.0257	1032.80542	14.43577	12.7589

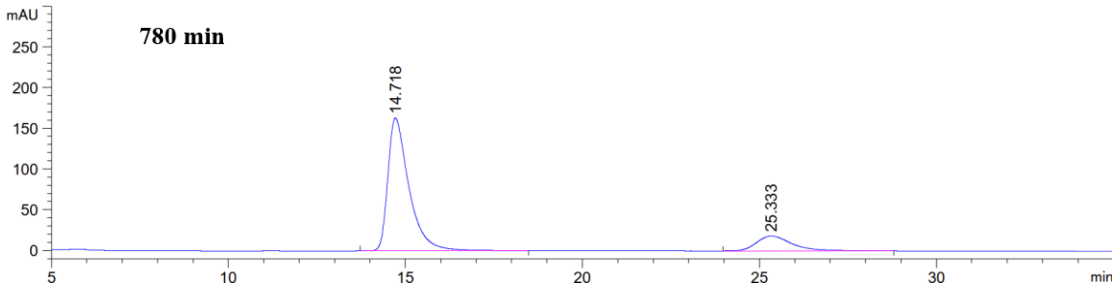


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.698	BB	0.6081	6860.38525	168.11638	86.2777
2	25.593	BB	1.0608	1091.13000	15.23152	13.7223

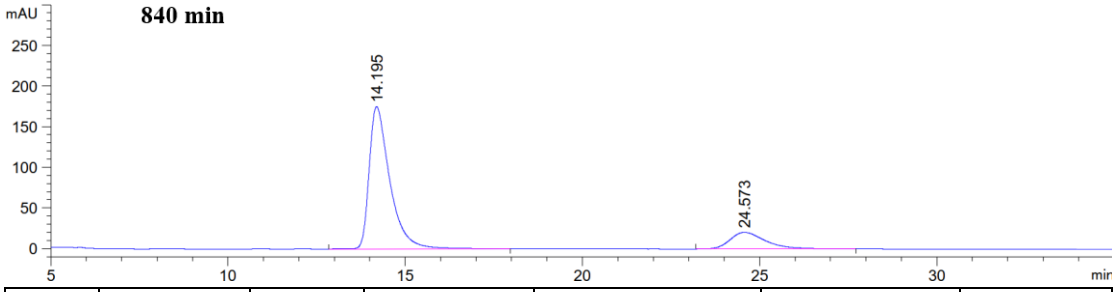


Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.598	BB	0.6030	7042.47168	173.32211	85.1850

2	25.333	BB	1.0673	1224.77905	17.06495	14.8150



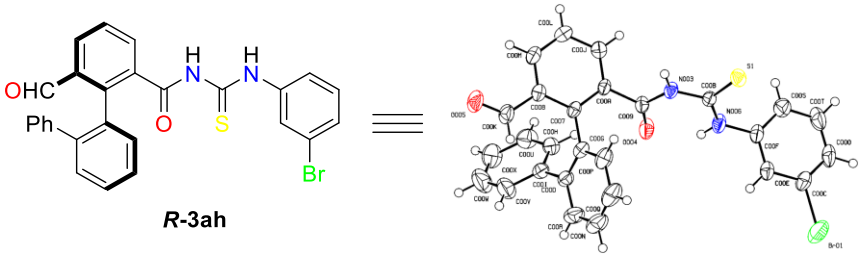
Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.718	BB	0.6165	6761.50049	163.14734	84.1910
2	25.333	BB	1.0560	1269.64514	18.17545	15.8090



Peak	PetTime	Type	Width(min)	Area(mAU*S)	Hight(mAU)	Area%
1	14.195	BB	0.6052	7086.54688	175.08601	83.3540
2	24.573	BB	1.0276	1415.20117	20.39286	16.6460

VI. X-Ray Crystallographic Data

A single crystal of **3ah** suitable for X-ray crystallography was obtained by crystallization *via* evaporation from its hexane/^{i}PrOH solution. And the crystal structure of compound **3ah** has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2223845).



***R*-3ah**

Bond precision: C-C = 0.0080 A Wavelength = 1.54178

Cell: a = 9.2241(8) b = 10.399(1) c = 25.056(2)

alpha = 90 beta = 90 gamma = 90

Temperature: 287 K Crystal system：orthorhombic Radiation：CuK\a (λ = 1.54178)

Crystal size/mm^3： 0.30 × 0.25 × 0.25 Index ranges：-10 ≤ h ≤ 9, -6 ≤ k ≤ 11, -29 ≤ l ≤ 29

Independent reflections：3816 [R_{int} = 0.0313, R_{sigma} = 0.0394]

	Calculated	Reported
Volume	2403.4(4)	2403.4(4)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	$C_{27}H_{19}BrN_2O_2S$	$2(C_{27}H_{19}BrN_2O_2S)$
Sum formula	$C_{27}H_{19}BrN_2O_2S$	$C_{54}H_{38}Br_2N_4O_4S_2$
Mr	515.40	1030.82
Dx, g cm^{-3}	1.424	1.424
Z	4	2
Mu (mm-1)	3.356	3.356
F000	1048.0	1048.0
F000’	1049.09	
h, k, lmax	10, 12, 29	10, 11, 29
Nref	3979 [2290]	3816
Tmin, Tmax	0.420, 0.432	
Tmin’	0.318	

Correction method= Not given

Data completeness = 1.67/0.96 Theta(max) = 63.862

R(reflections) = 0.0436 (3609) wR2(reflections) = 0.1150 (3816)

S = 1.071 Npar = 298

Flack parameter 0.092(10)

VII. References

[1] J. I. Urgel, M. D. Giovannantonio, K. Eimre, T. G. Lohr, J. Liu, S. Mishra, Q. Sun, A. Kinikar, R. Widmer, S. Stolz, M. Bommert, R. Berger, P. Ruffieux, C. A. Pignedoli, K. Mullen, X. Feng and R. Fasel, On-Surface Synthesis of Cumulene-Containing Polymers via Two-Step Dehalogenative Homocoupling of Dibromomethylene-Functionalized Tribenzoazulene, *Angew. Chem., Int. Ed*., 2020, **59**,13281-13287.

[2] (a) T. Fukuzumi and J. W. Bode, A Reagent for the Convenient, Solid-Phase Synthesis of N-Terminal Peptide Hydroxylamines for Chemoselective Ligations, *J. Am. Chem. Soc*., 2009, **131**, 3864-3865; (b) S. Staniland, B. Yuan, N. Gimnez-Agull, T. Marcelli, S. C. Willies, D. M. Grainger, N. J. Turner and J. Clayden, Enzymatic Desymmetrising Redox Reactions for the Asymmetric Synthesis of Biaryl Atropisomers, *Chem. Eur. J.,* 2014, **20**, 13084-13088.

[3] C. Rodríguez-Franco, E. Roldán-Molina, A. Aguirre-Medina, R. Fernández, V. Hornillos and J. M. Lassaletta, Catalytic Atroposelective Synthesis of C−N Axially Chiral Aminophosphines via Dynamic Kinetic Resolution, *Angew. Chem., Int. Ed*., 2024, **63**, e202409524.

[4] Y. Sawama, Y. Miki and H. Sajiki, N-Heterocyclic Carbene Catalyzed Deuteration of Aldehydes in D_2O, *Synlett,* 2020, **31**, 699-702.

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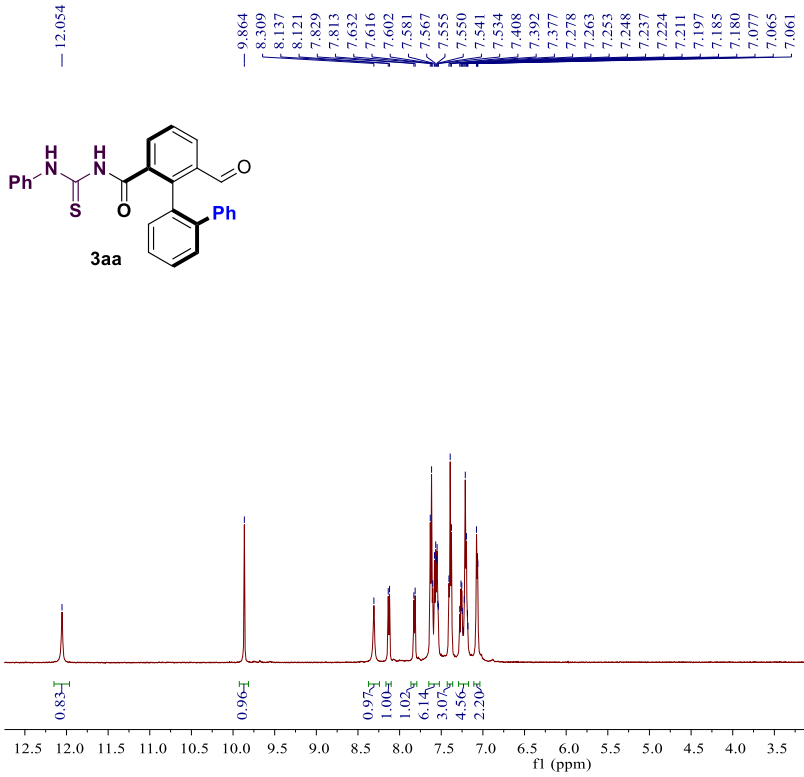
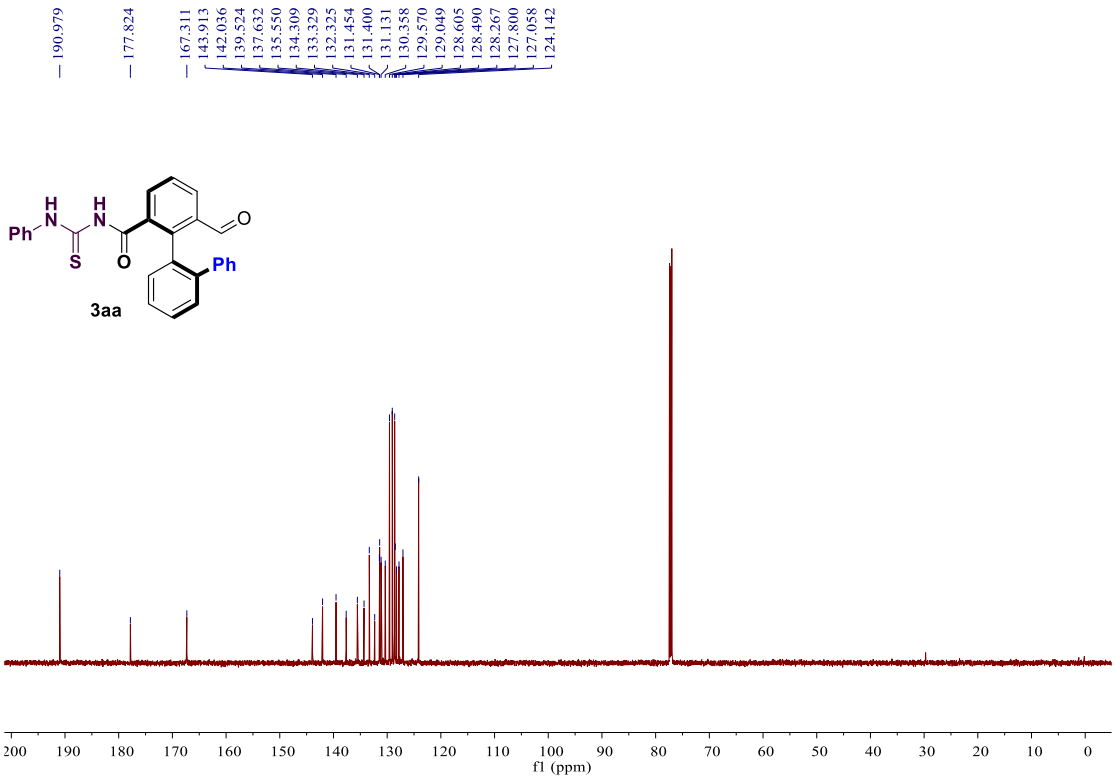
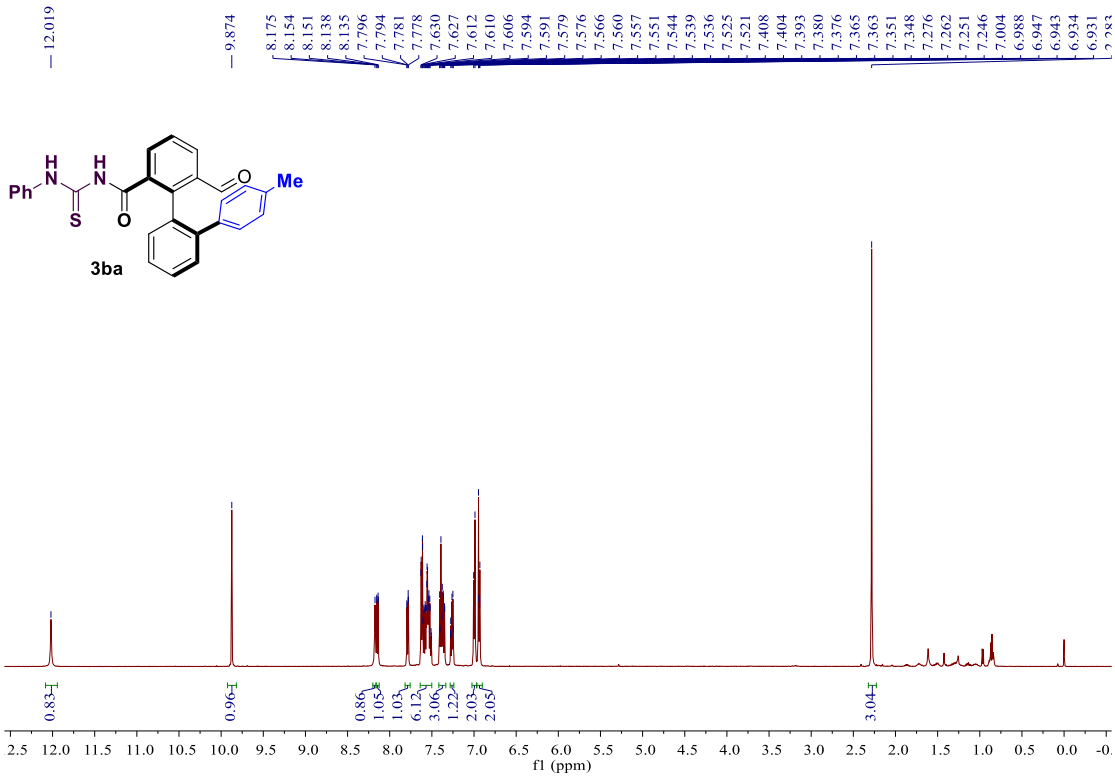
VIII. ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR Spectra of New Compounds.



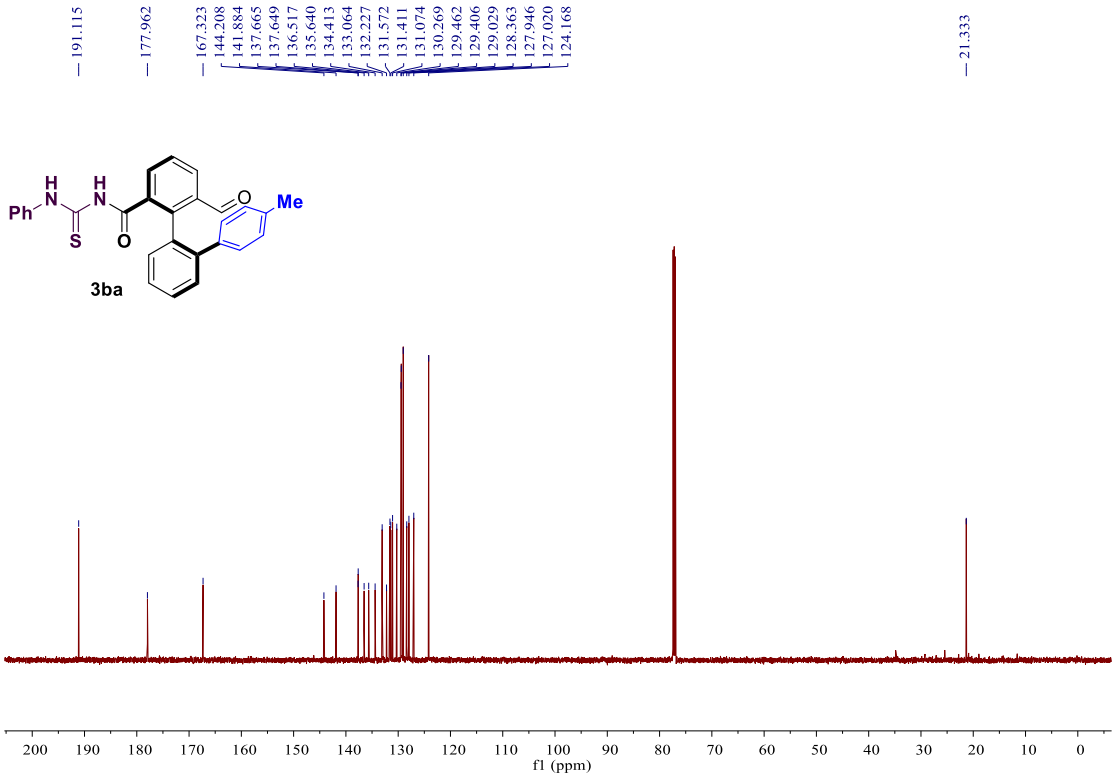
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aa.



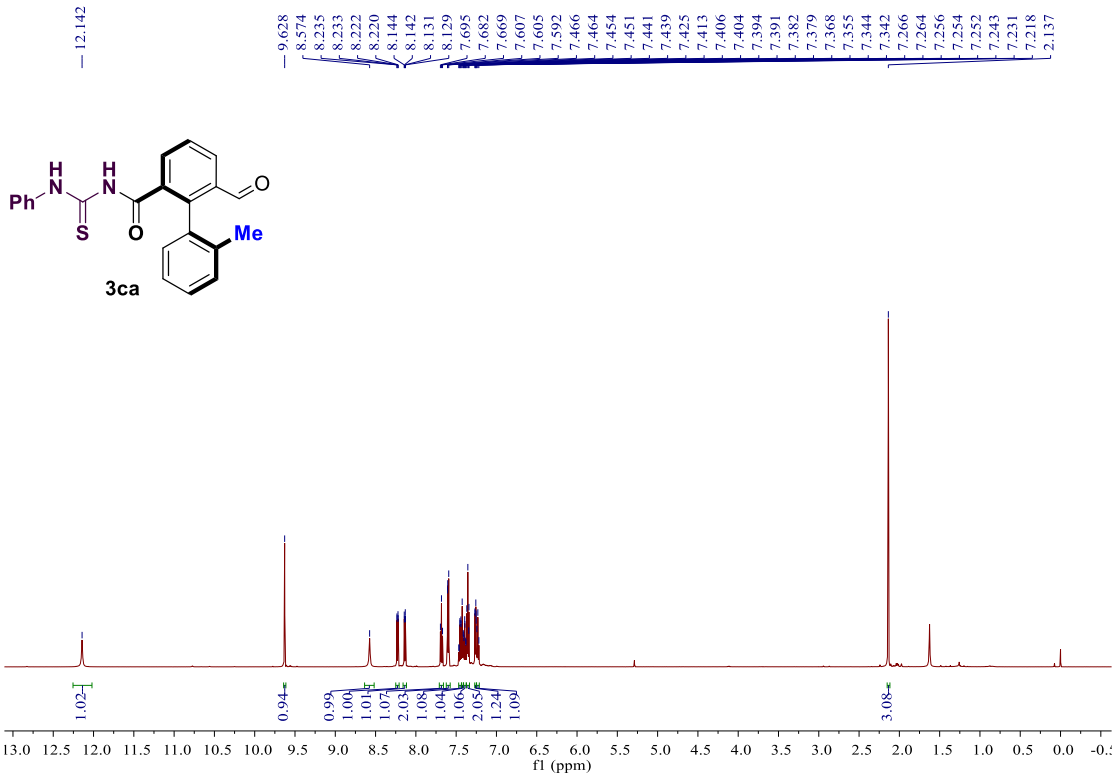
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3aa.



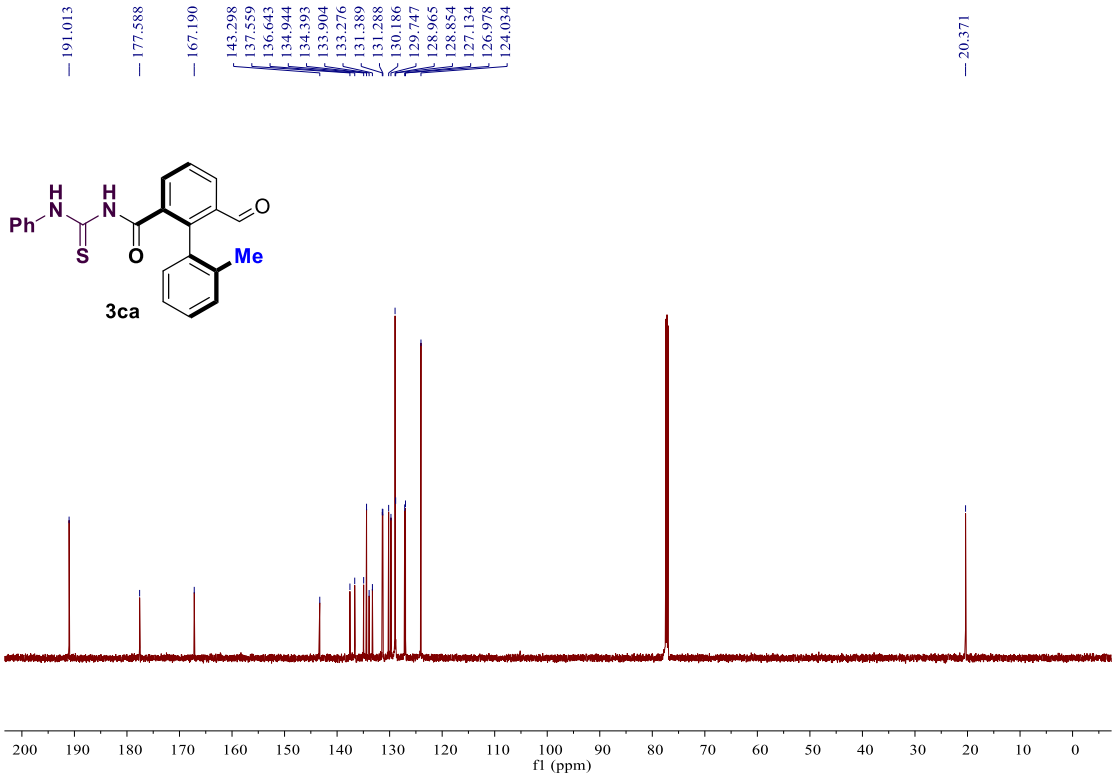
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ba.



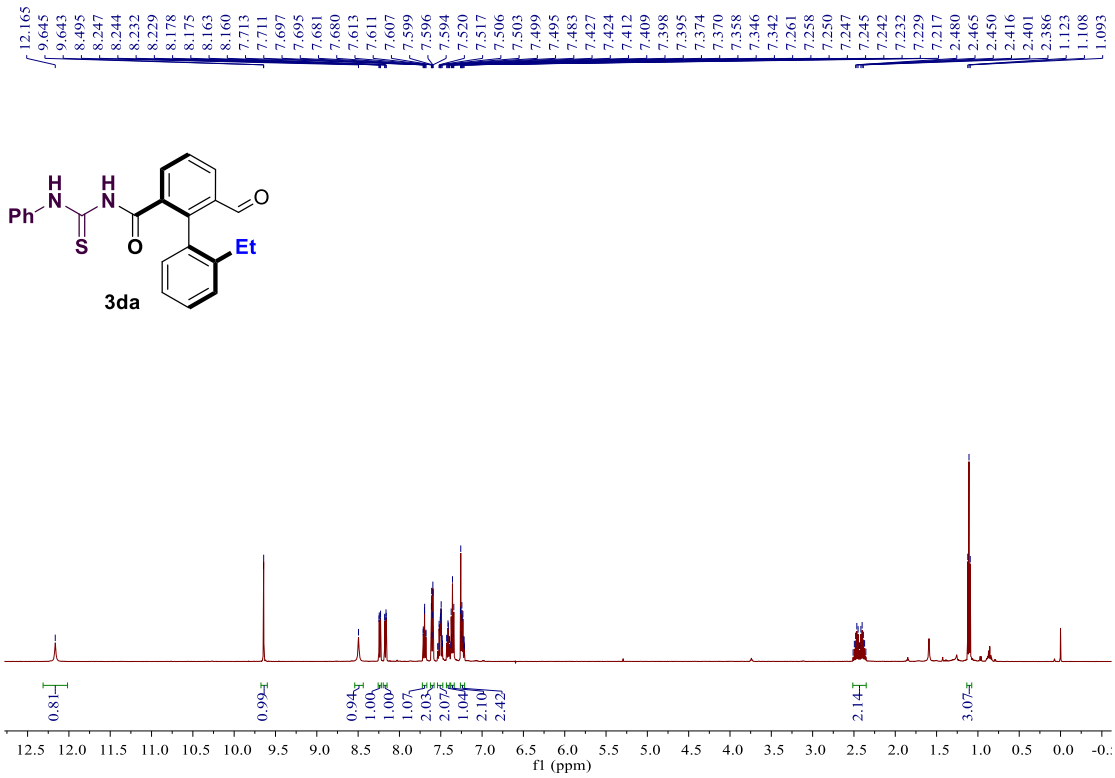
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ba.



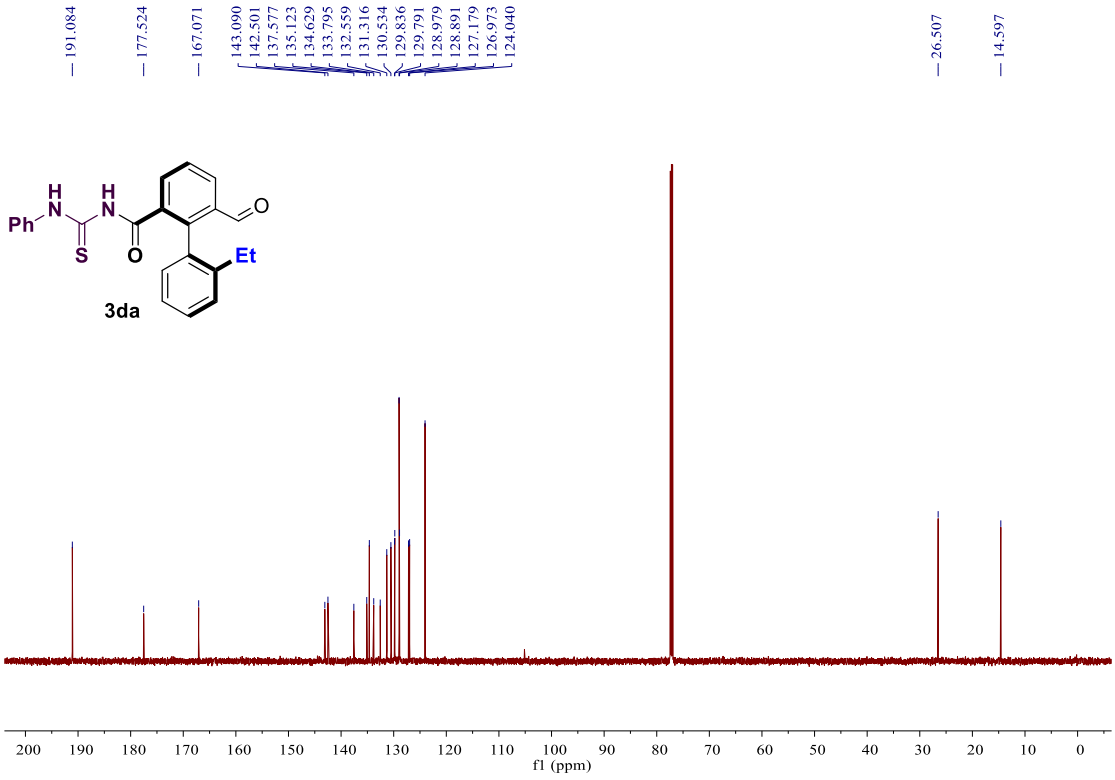
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ca.



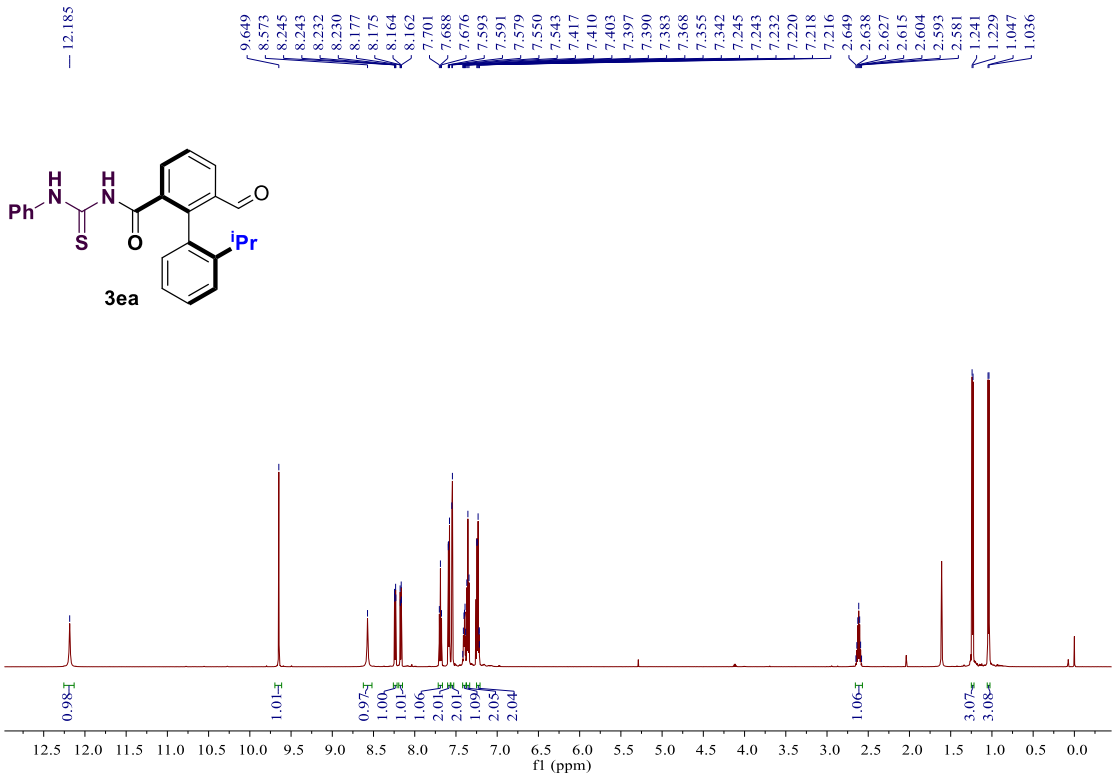
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ca.



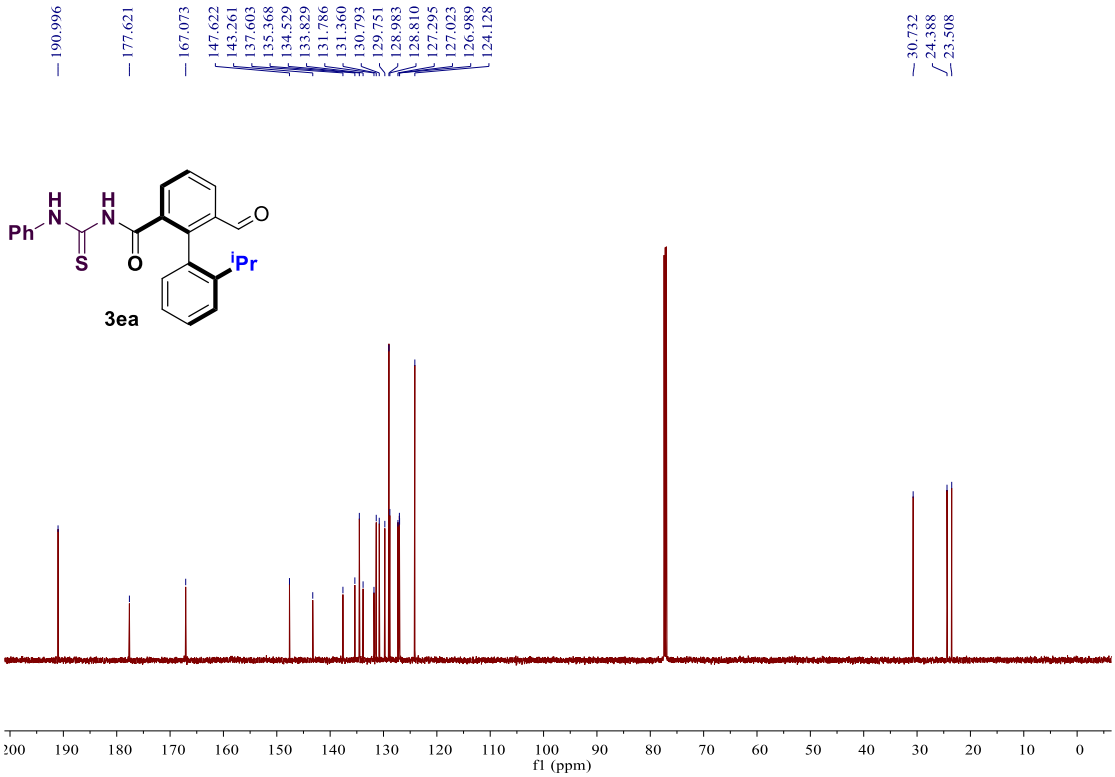
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3da.



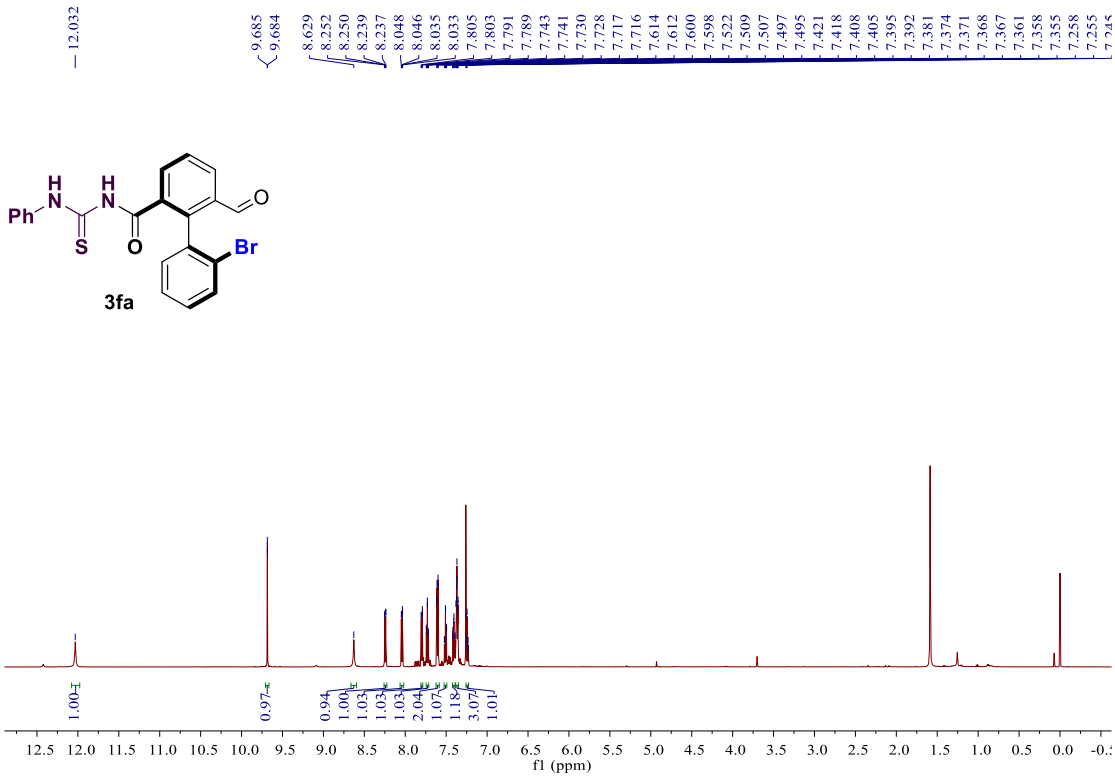
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3da.



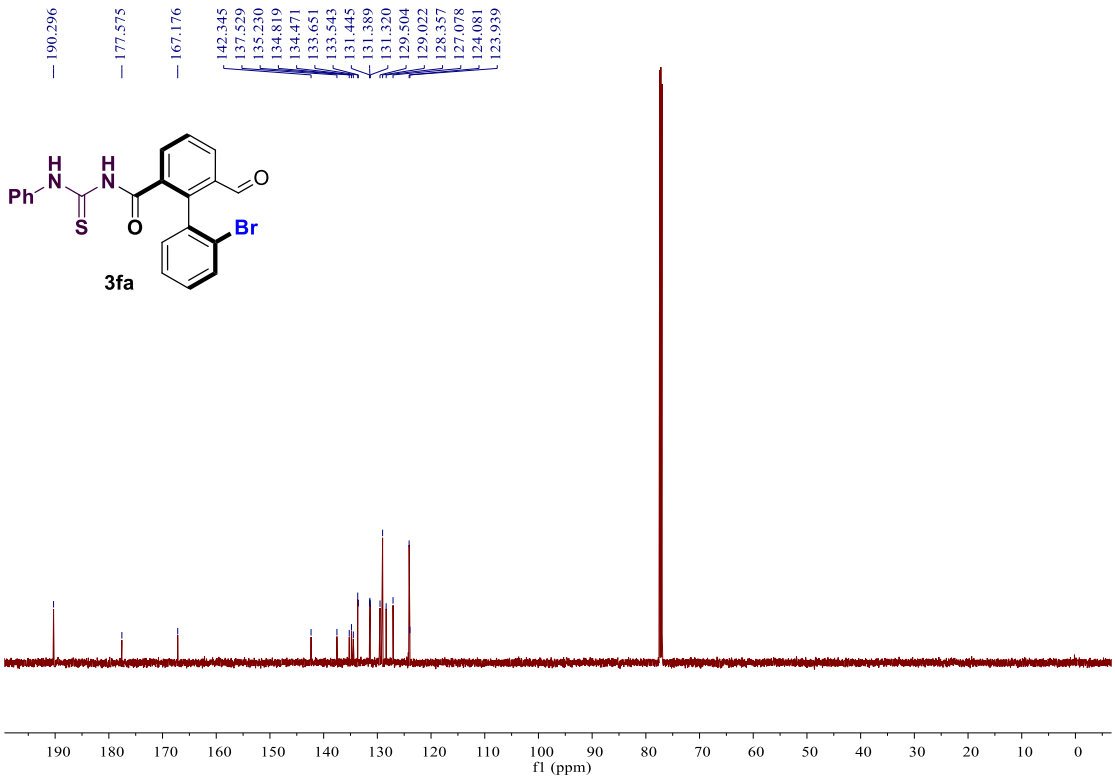
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ea.



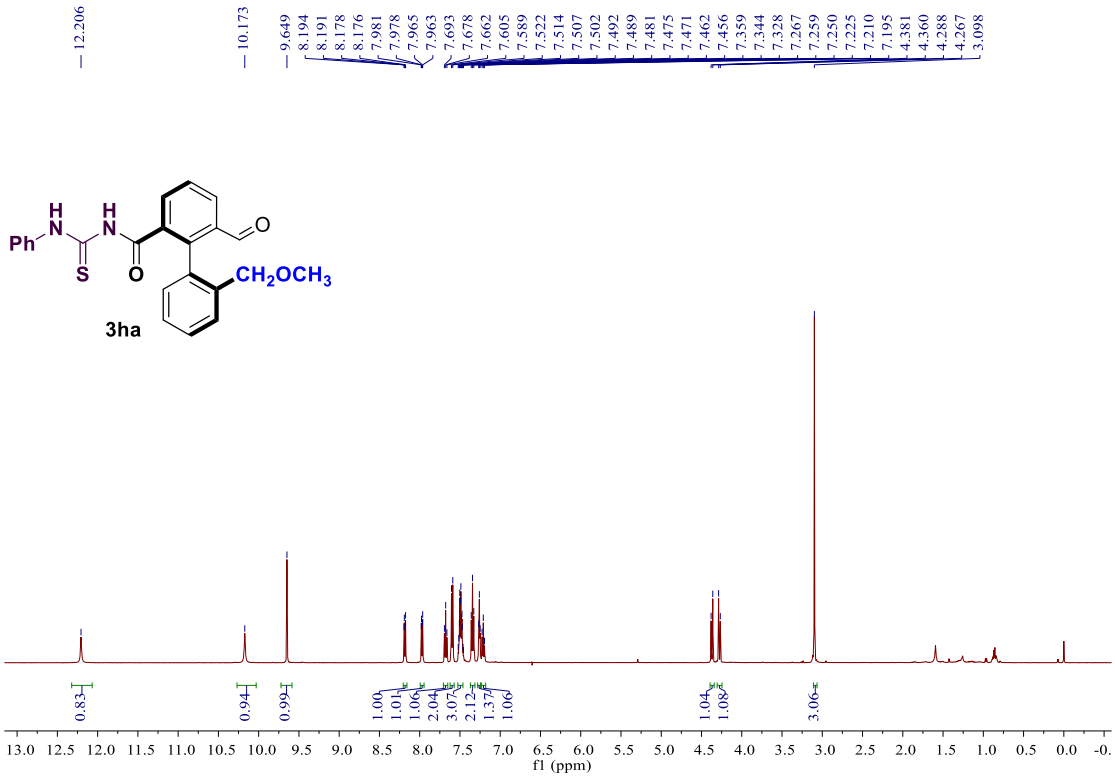
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ea.



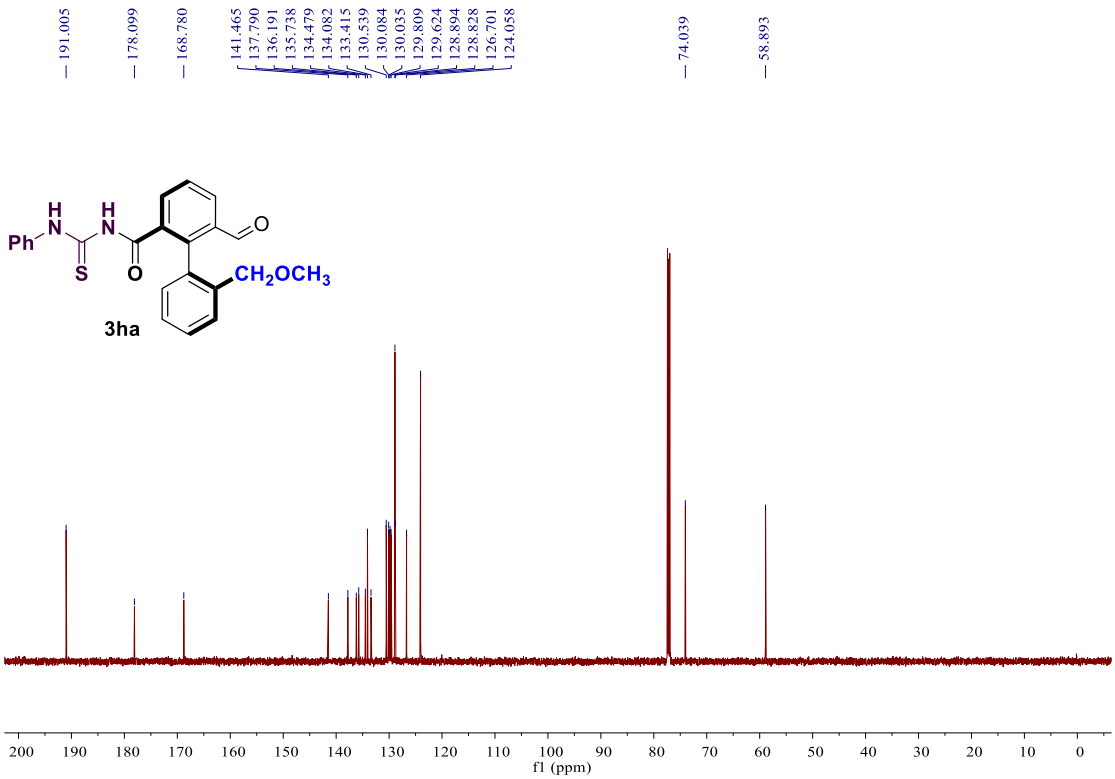
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3fa.



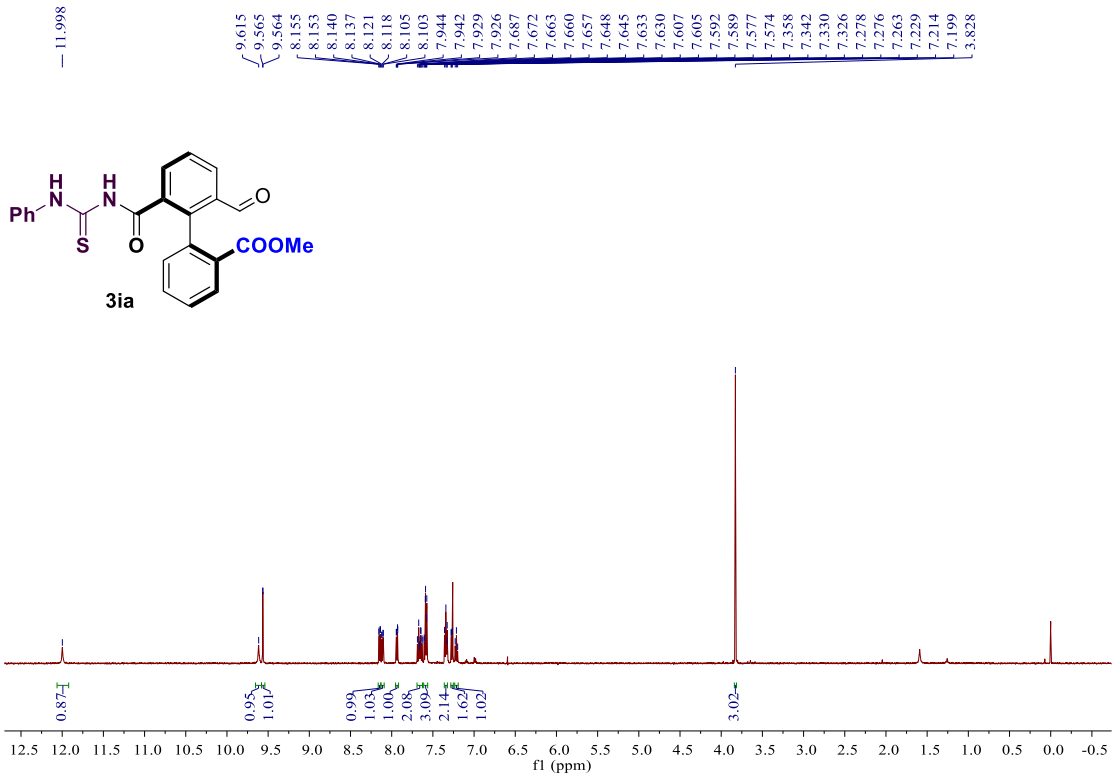
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3fa.



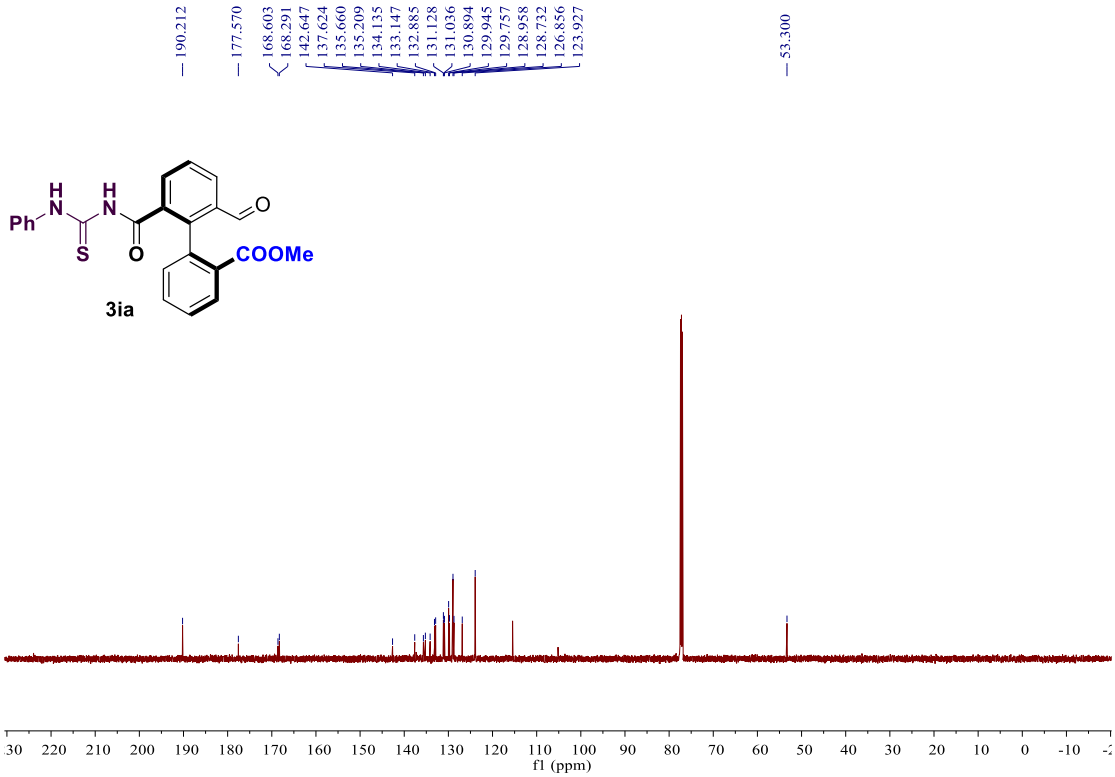
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ha.



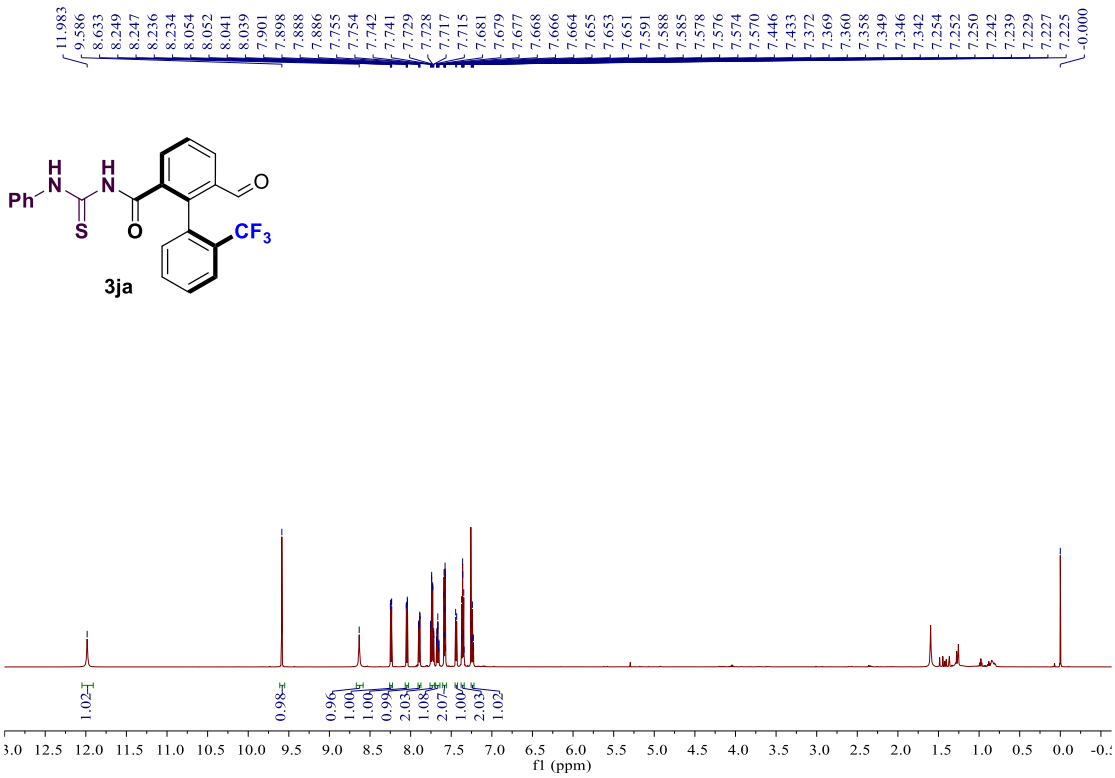
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ha.



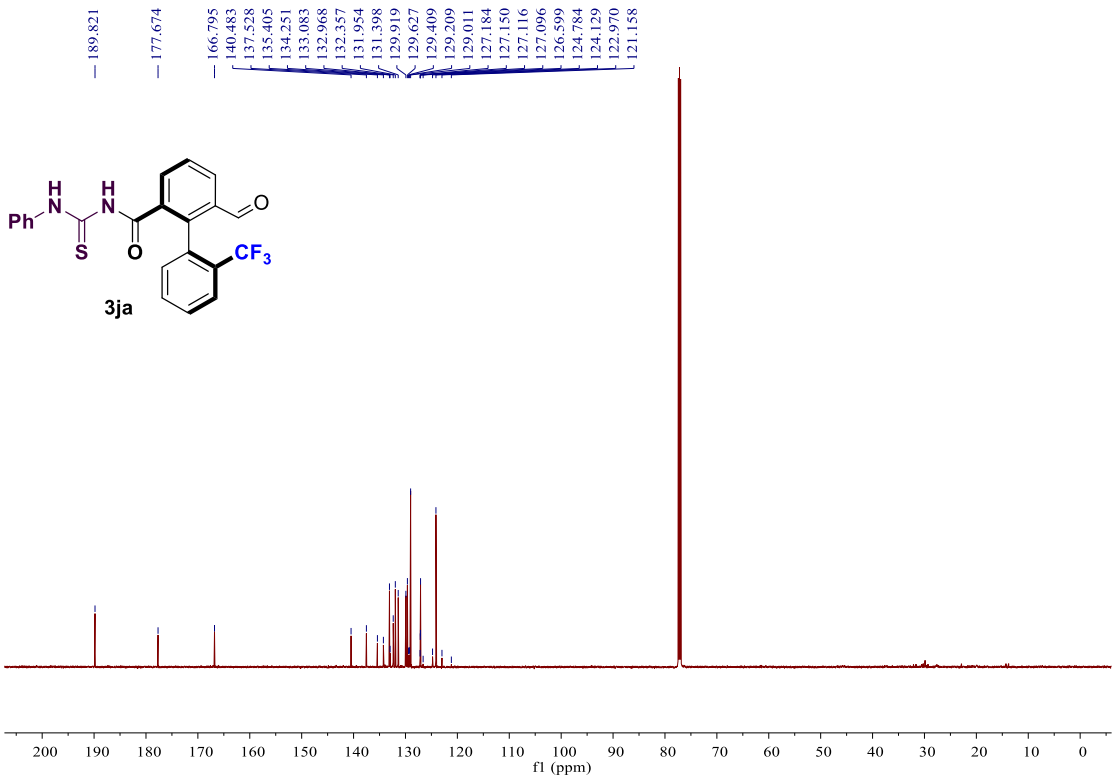
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ia.



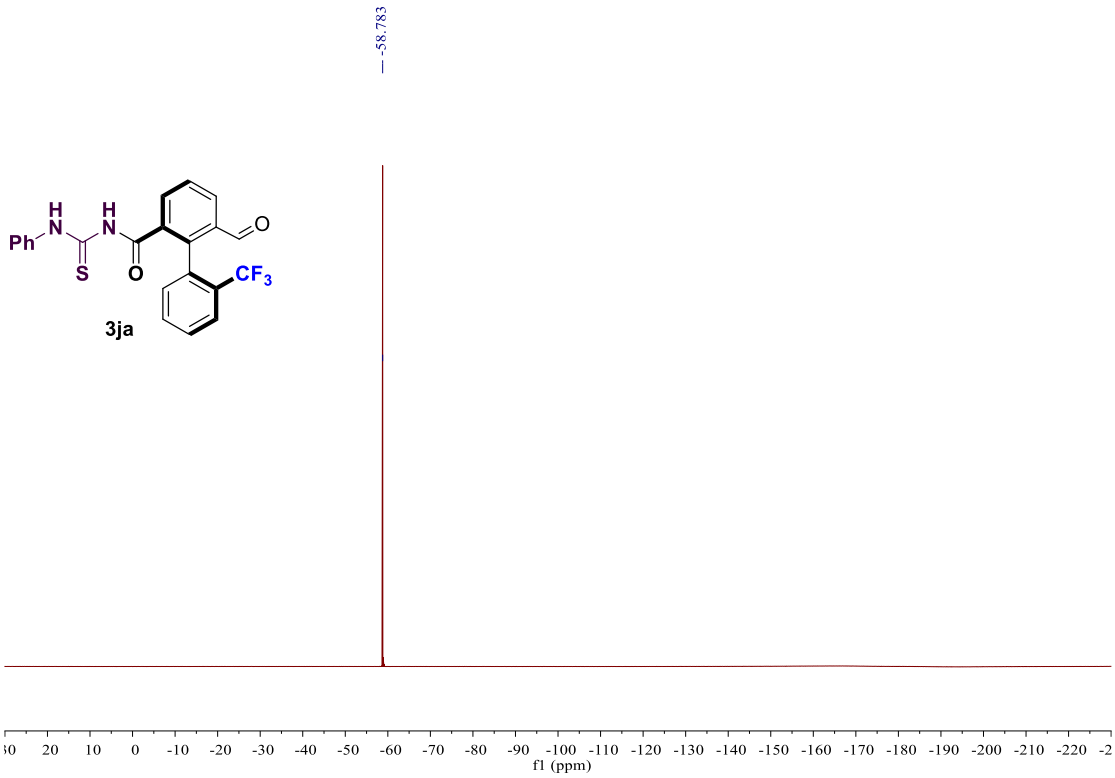
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ia.



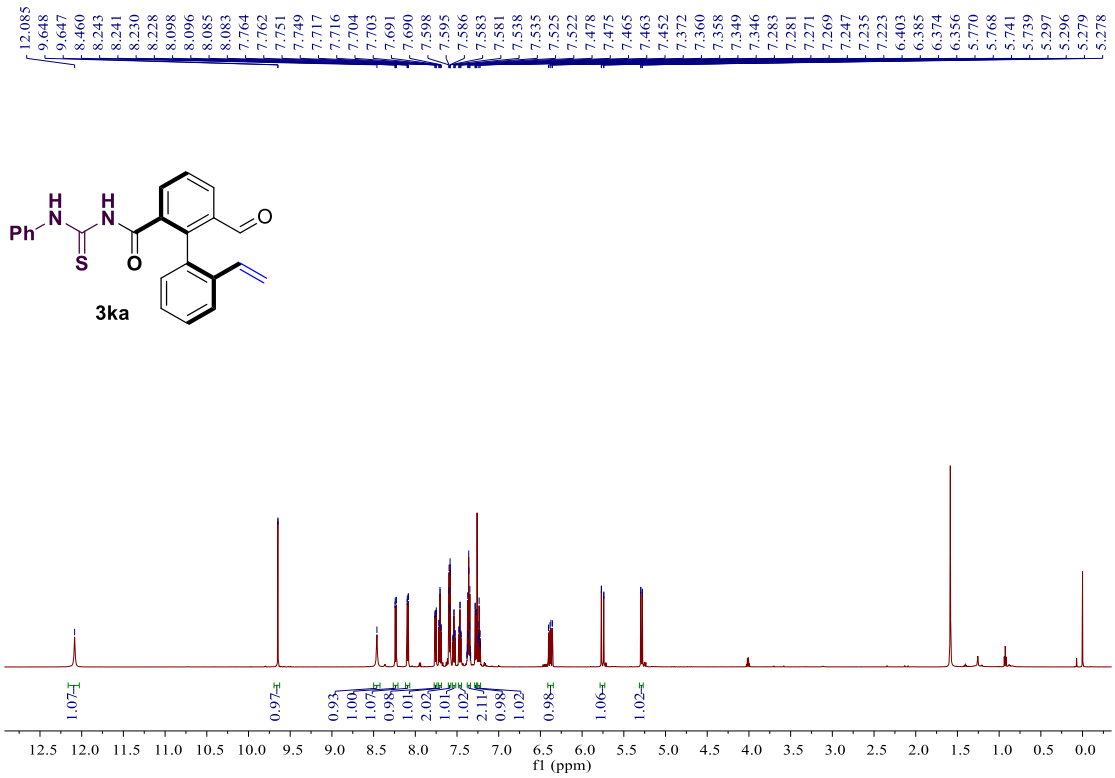
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ja.



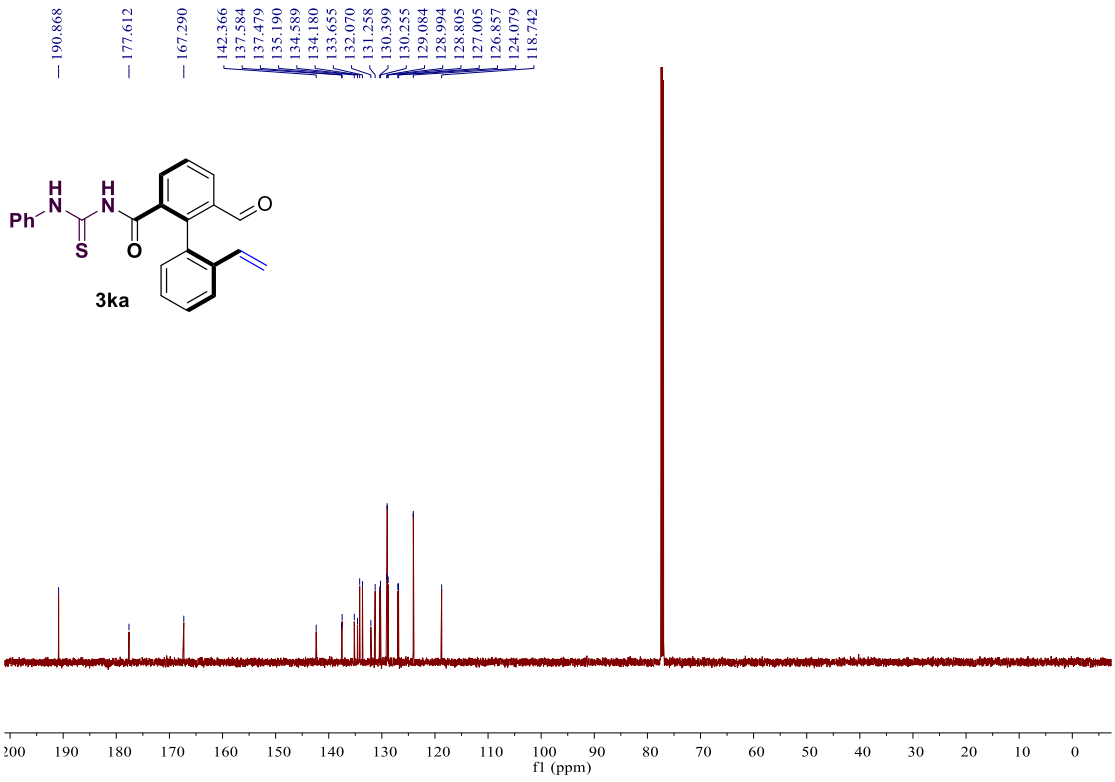
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ja.



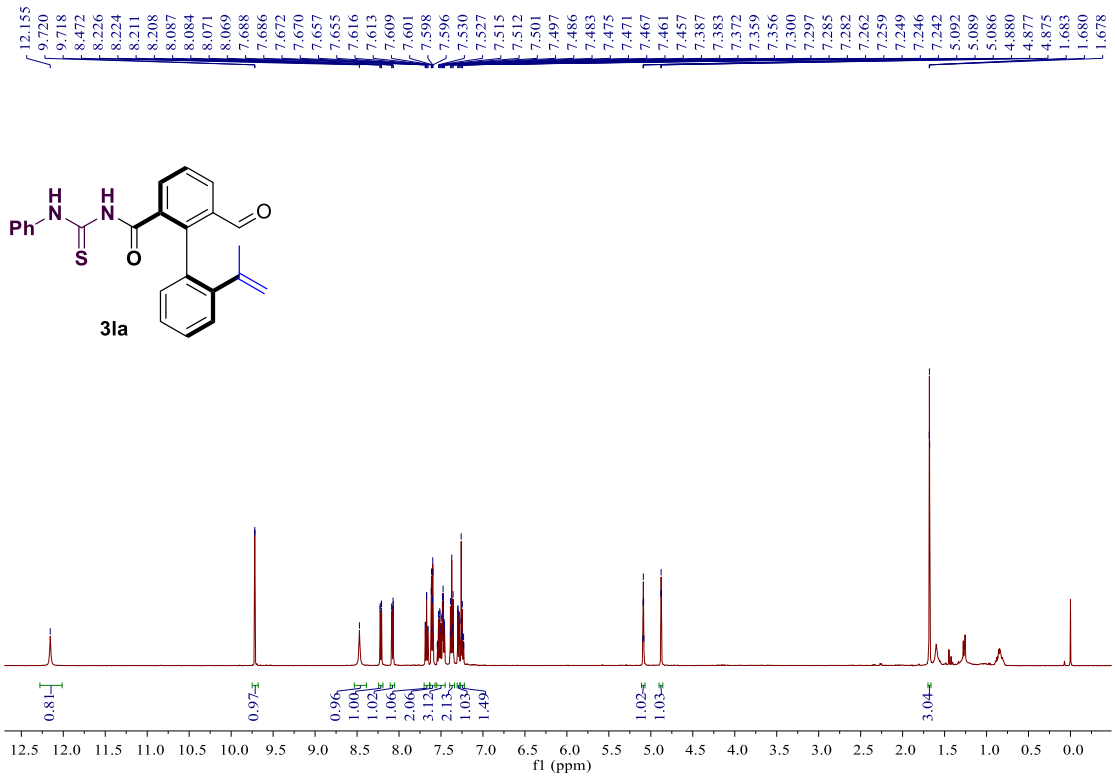
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3ja.



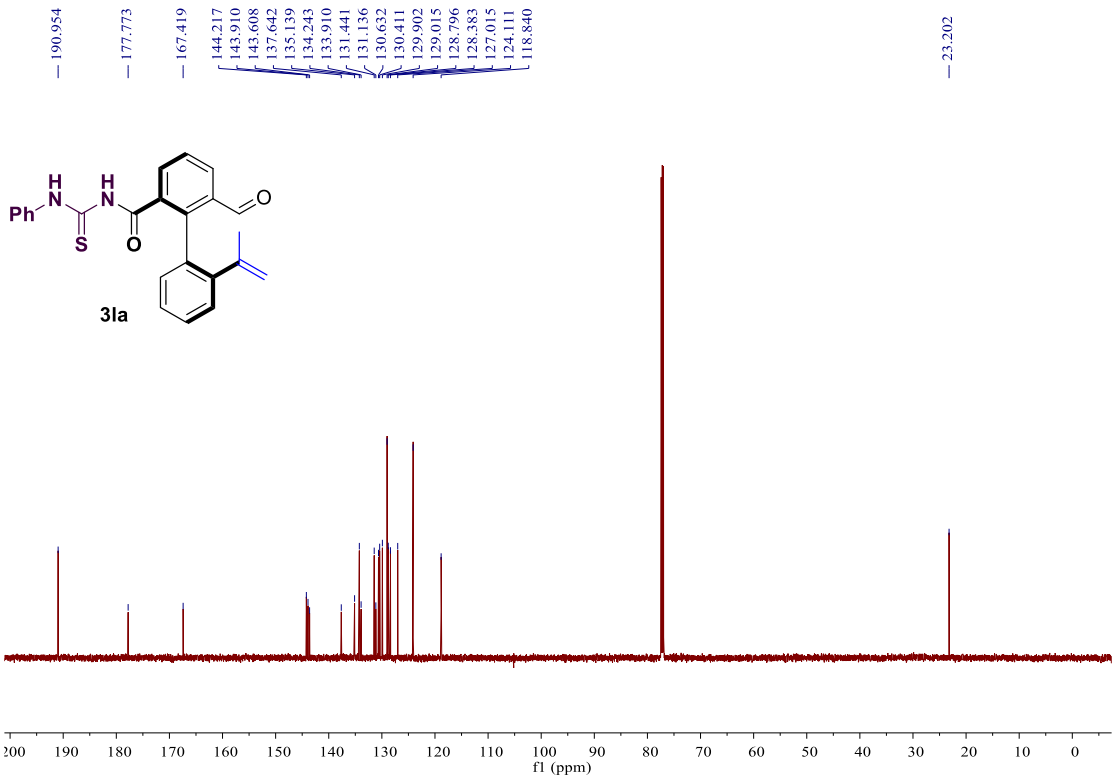
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ka.



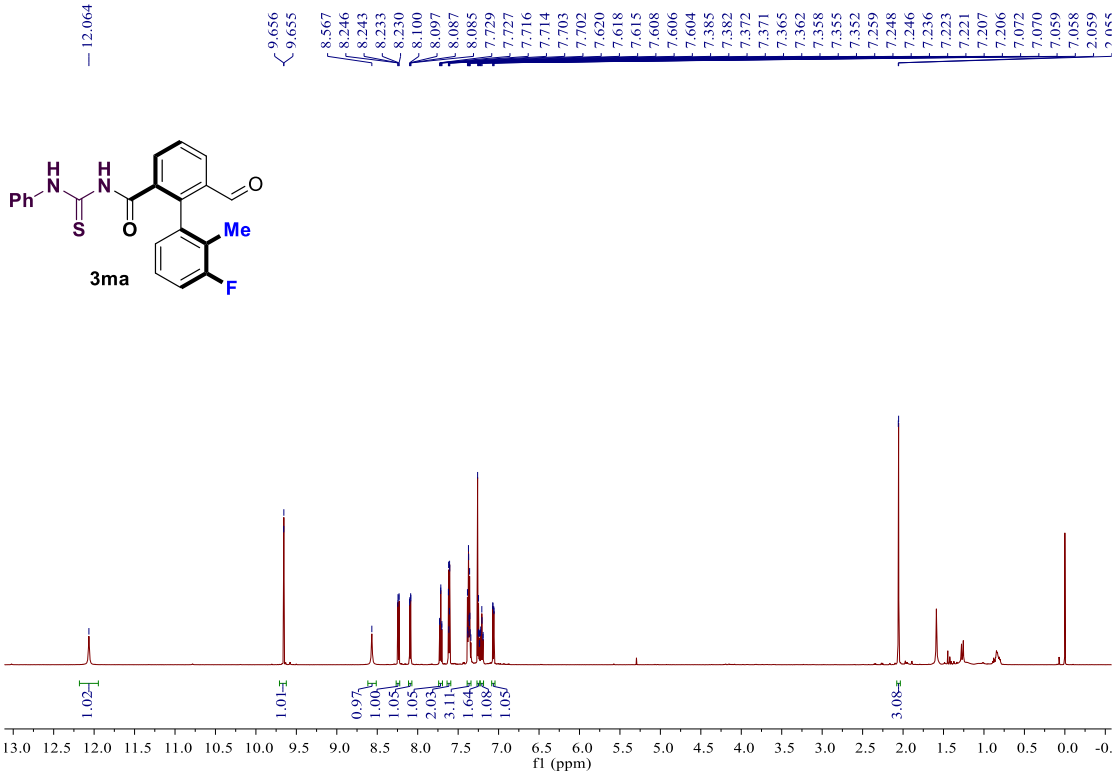
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ka.



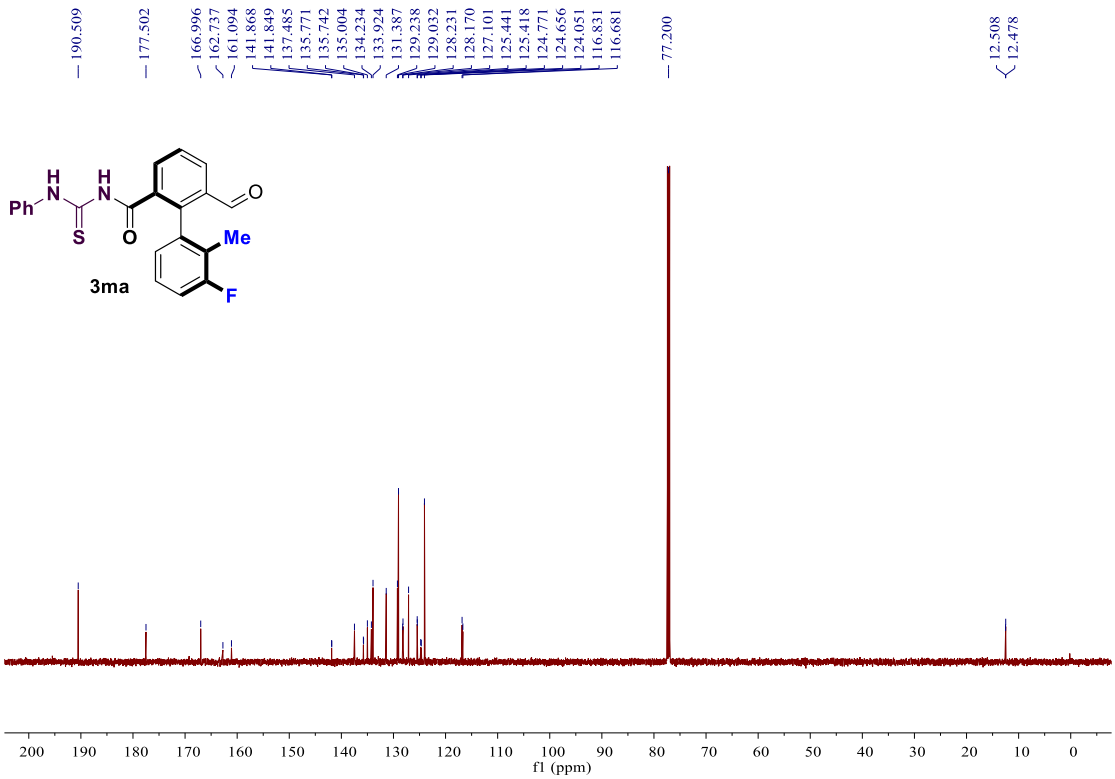
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3la.



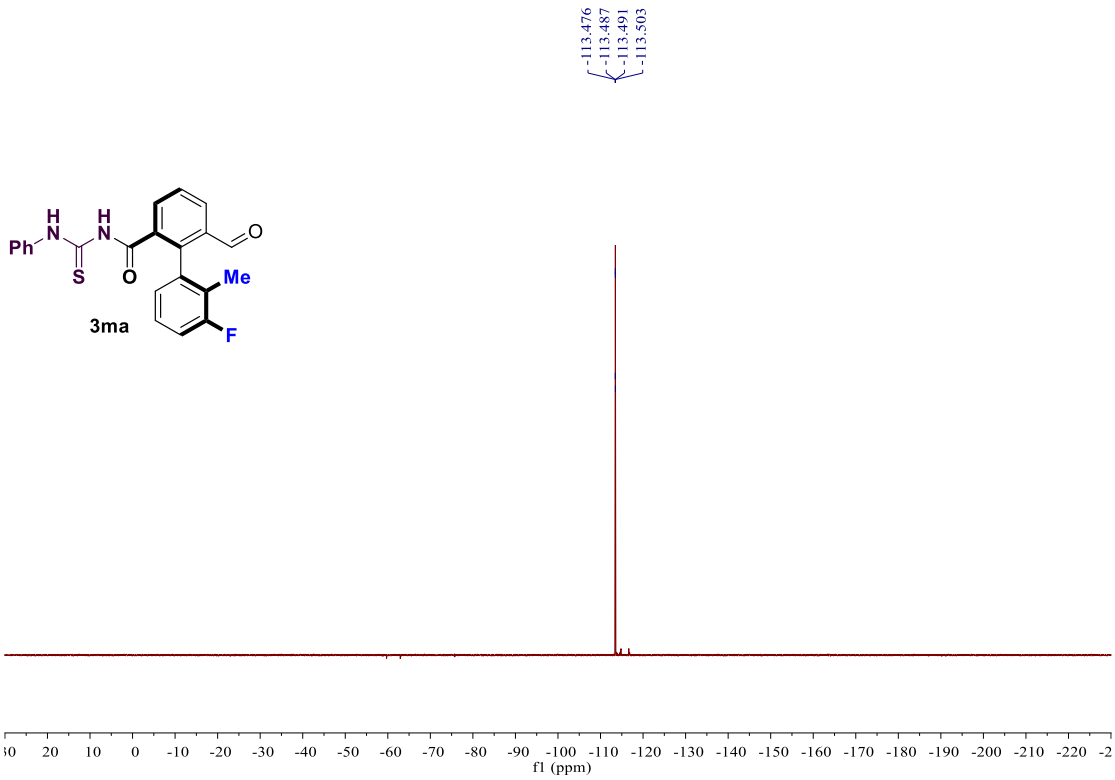
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3la.



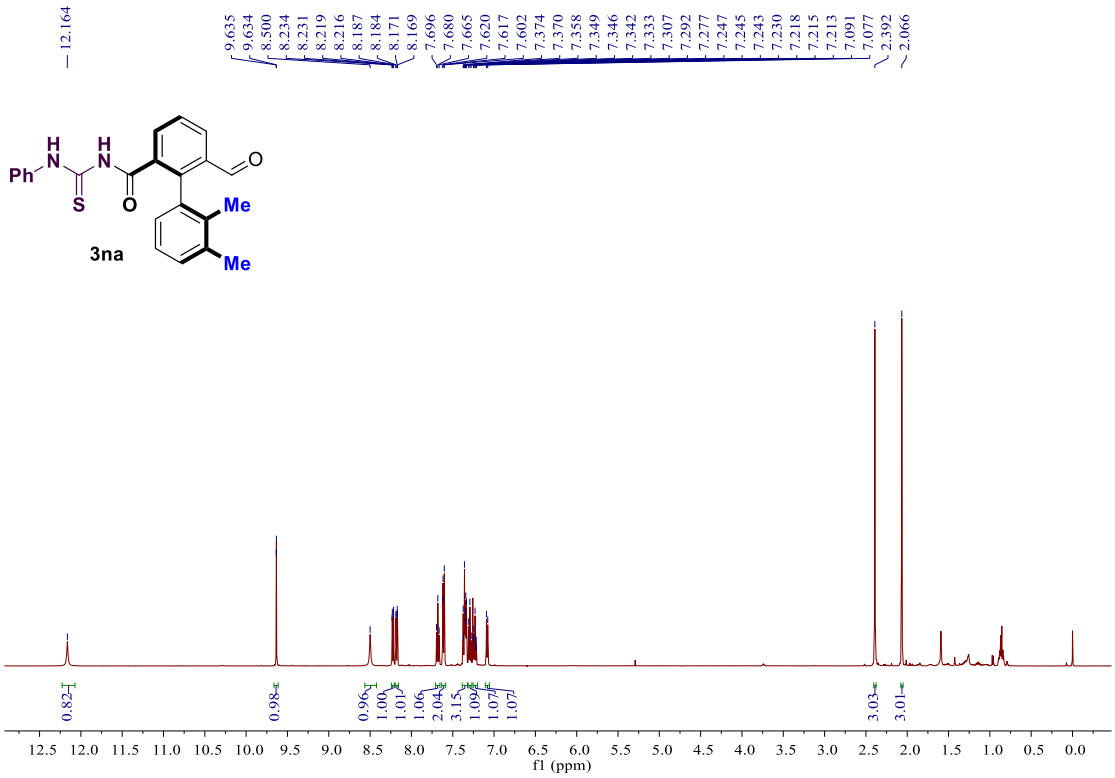
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3ma.



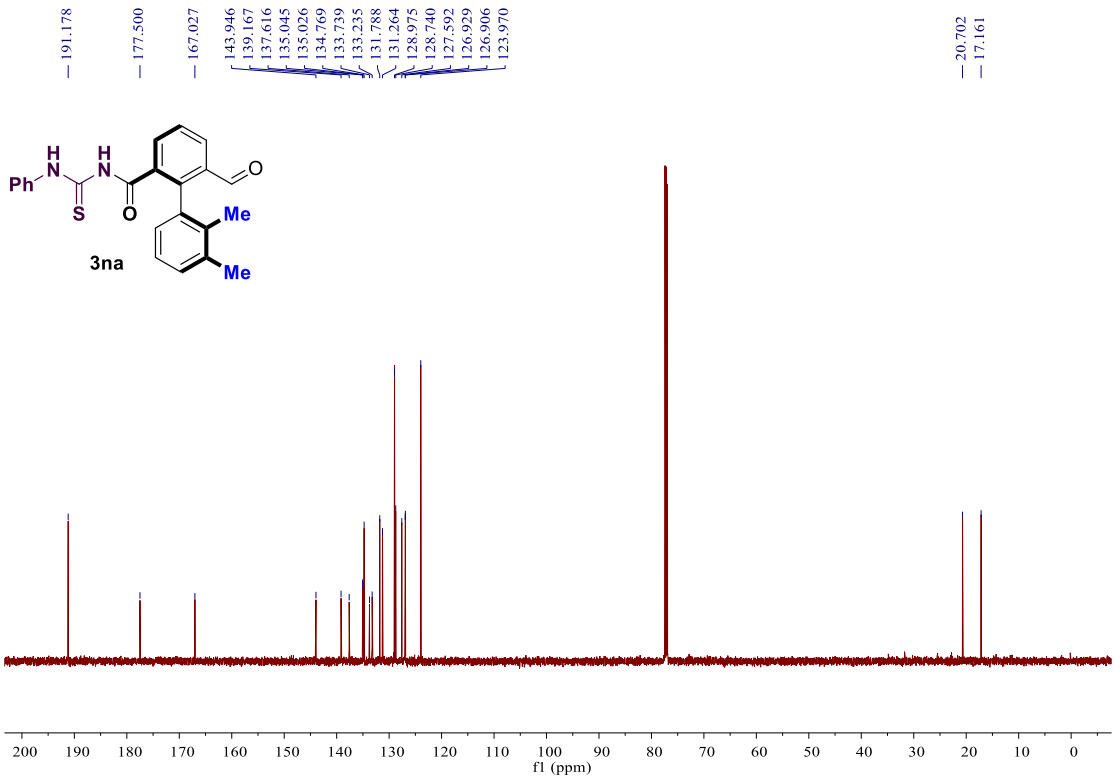
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ma.



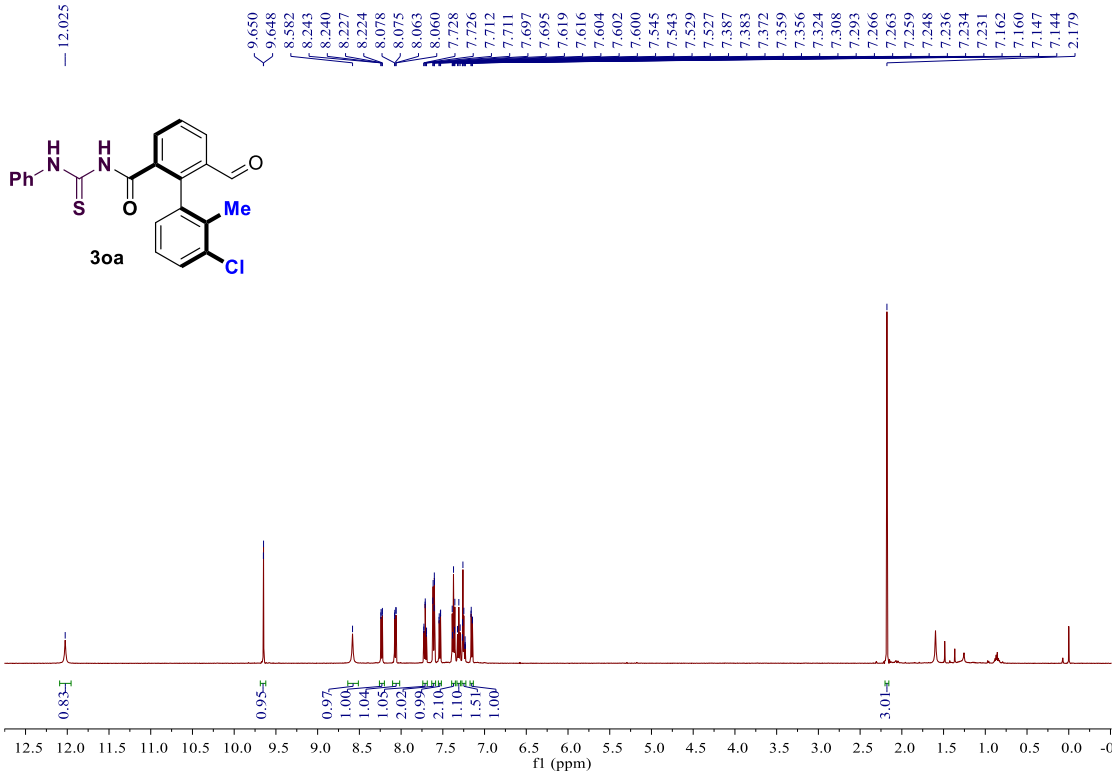
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3ma.



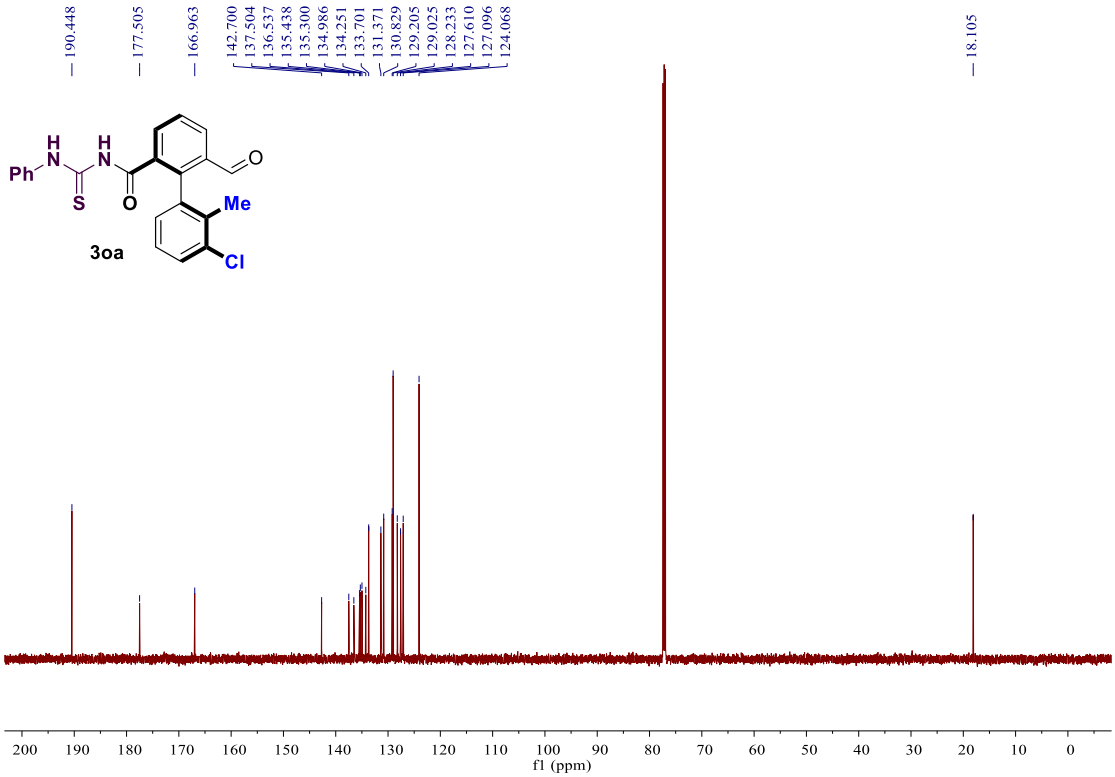
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3na.



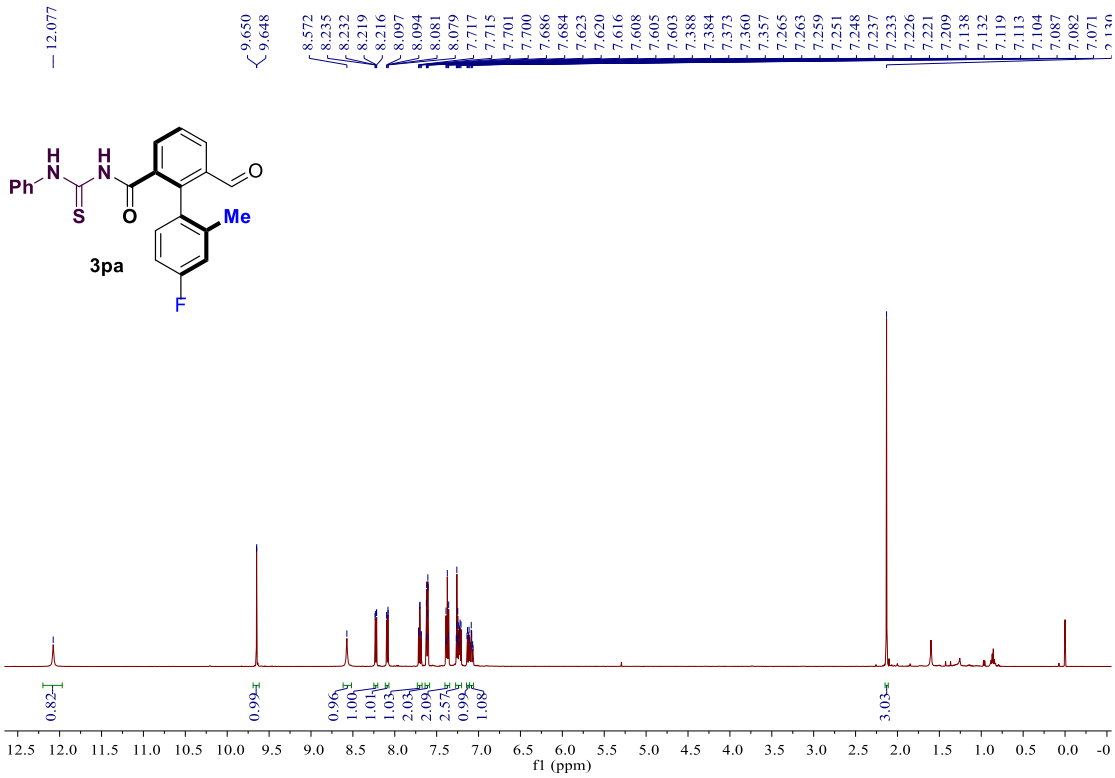
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3na.



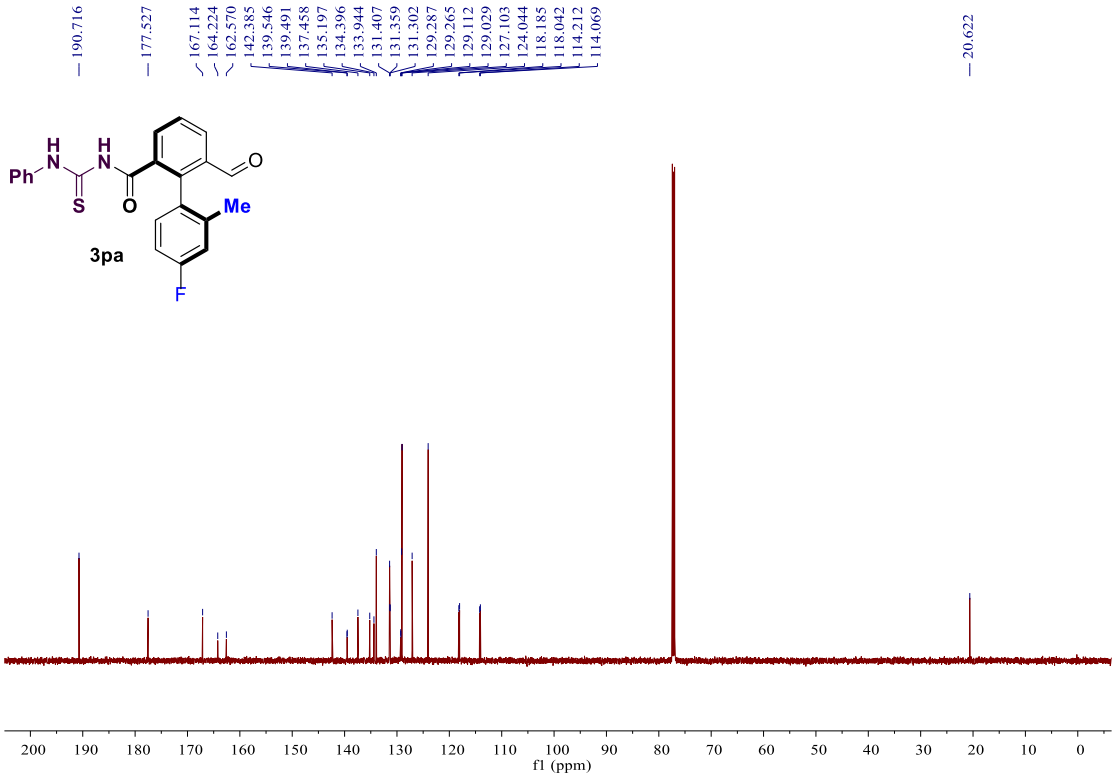
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3oa.



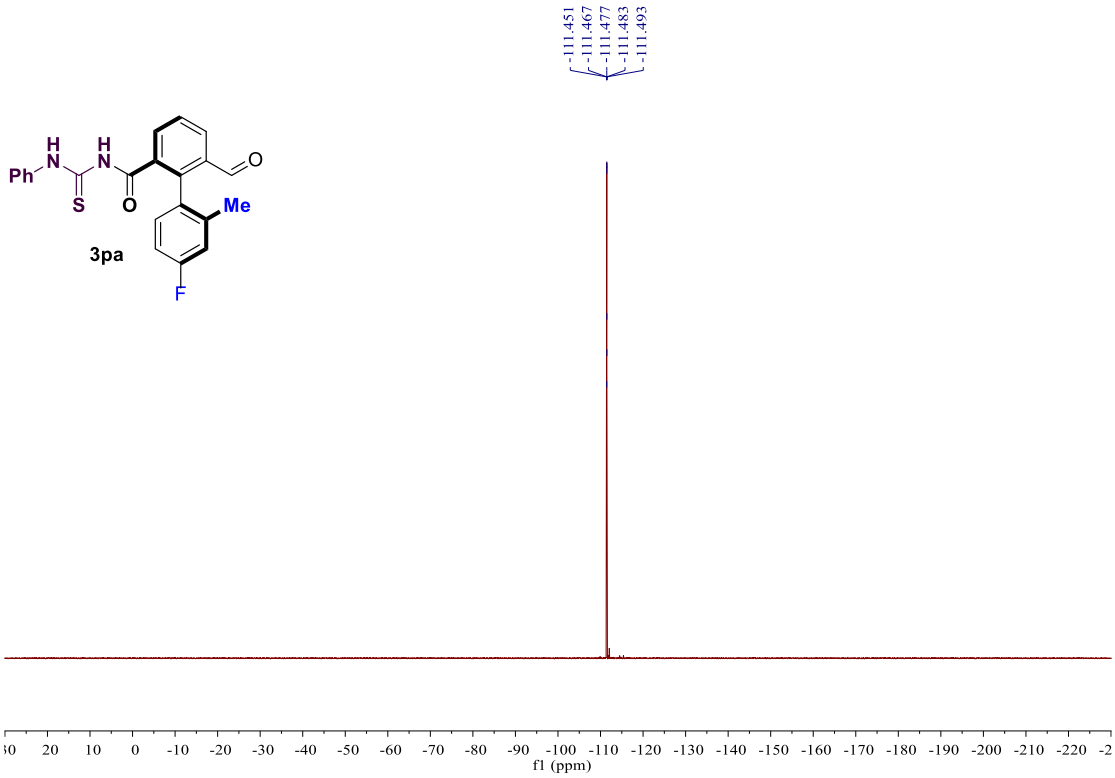
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3oa.



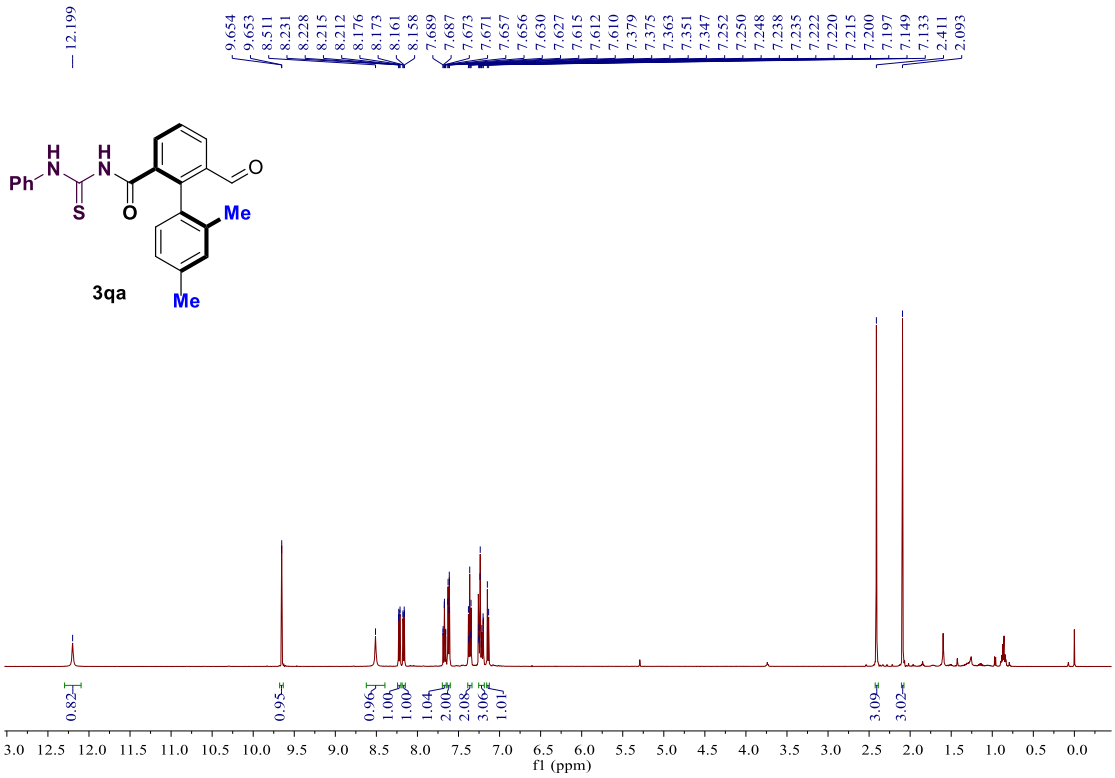
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3pa.



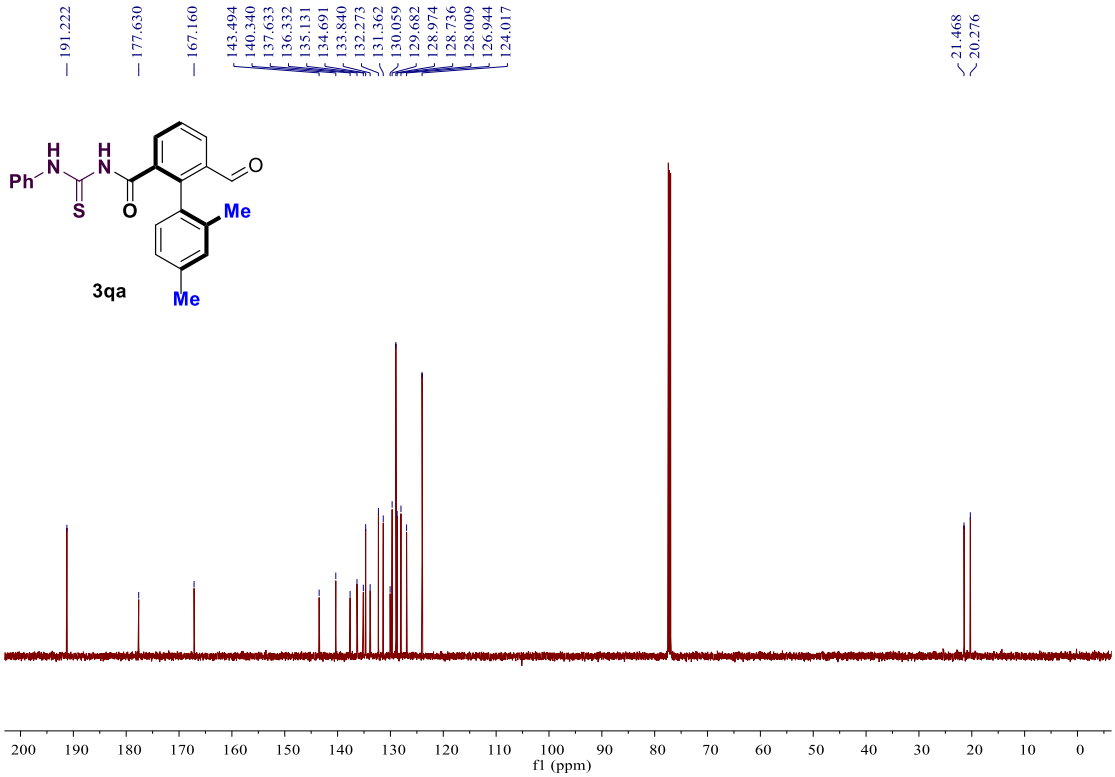
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3pa.



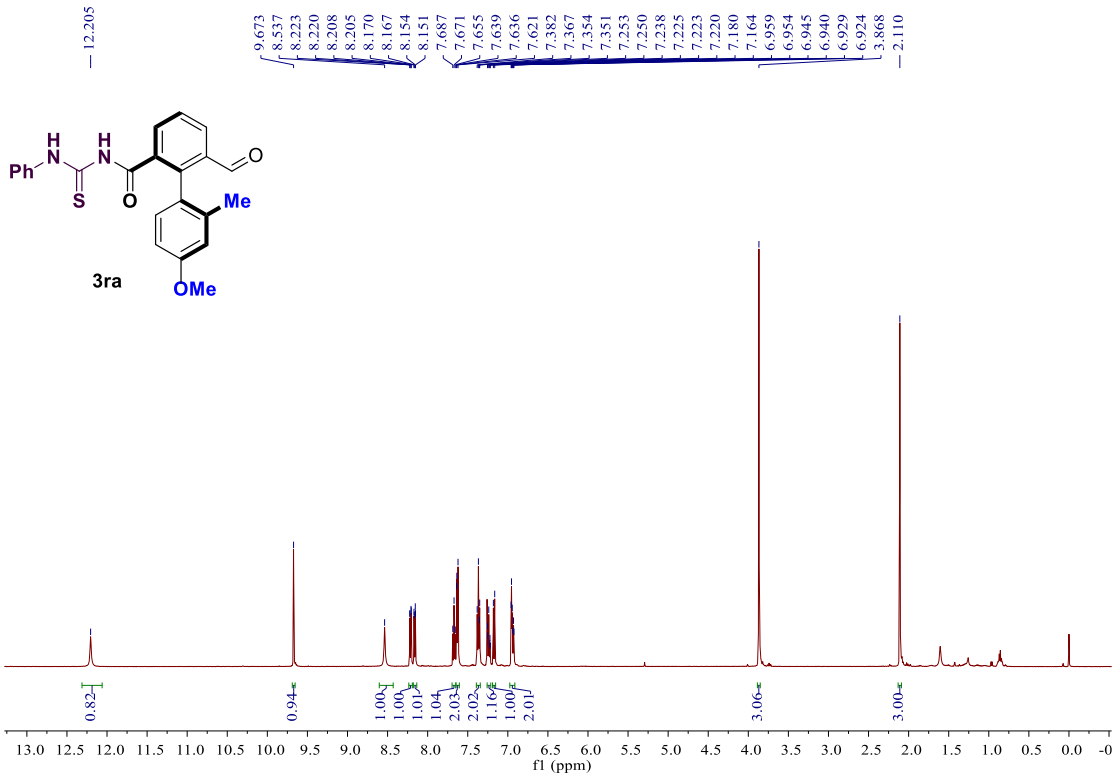
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3pa.



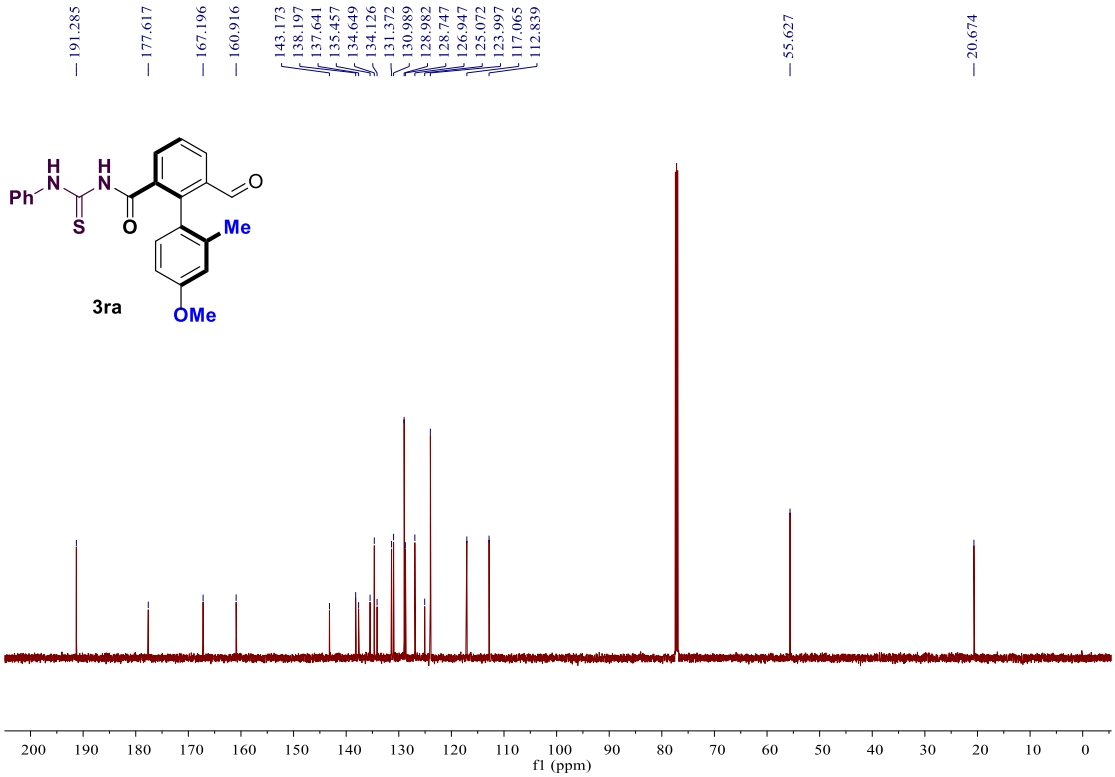
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3qa.



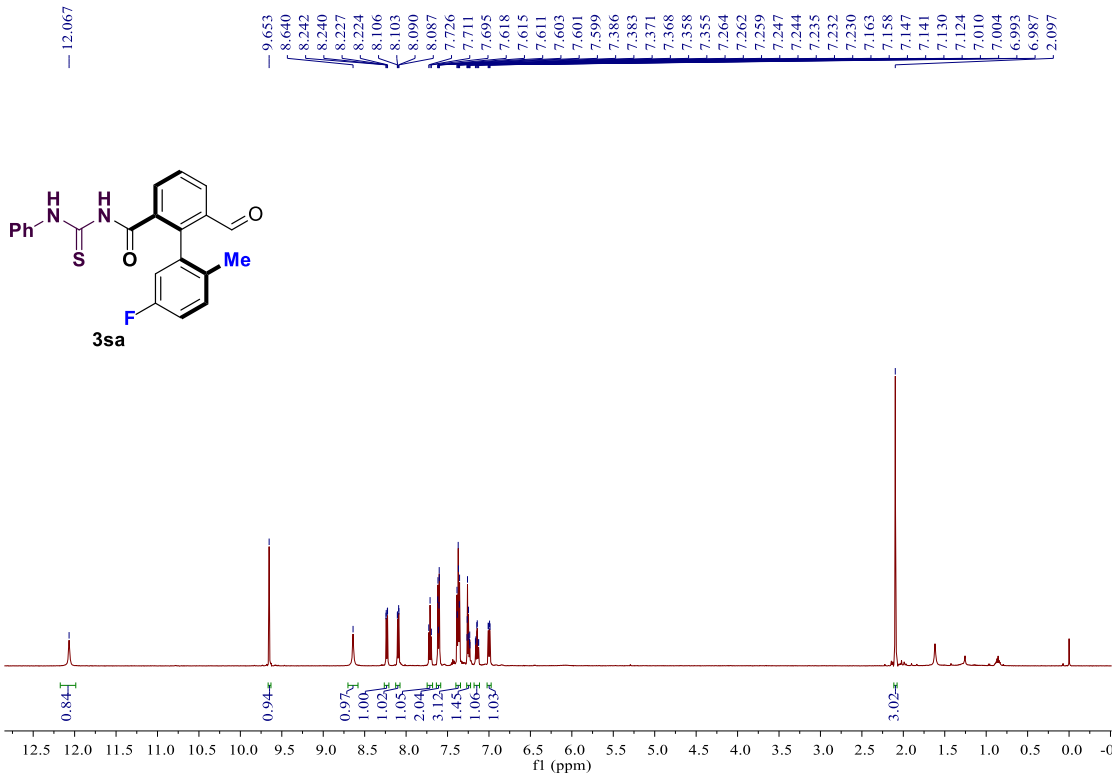
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3qa.



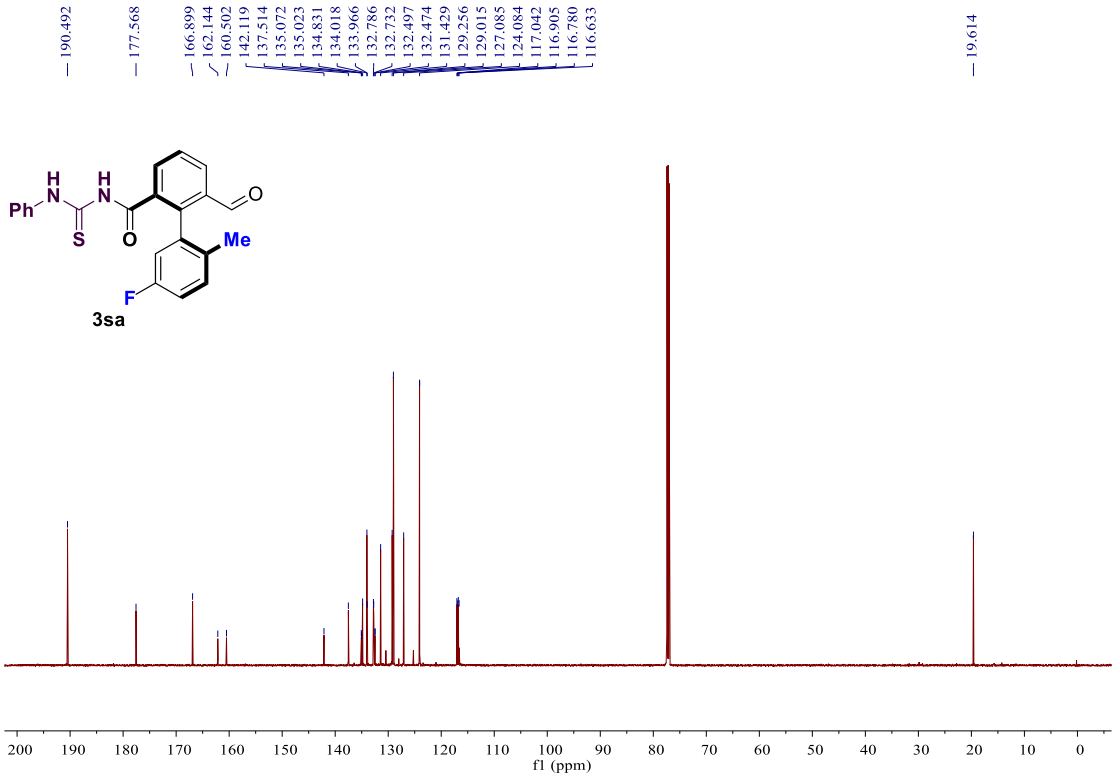
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ra.



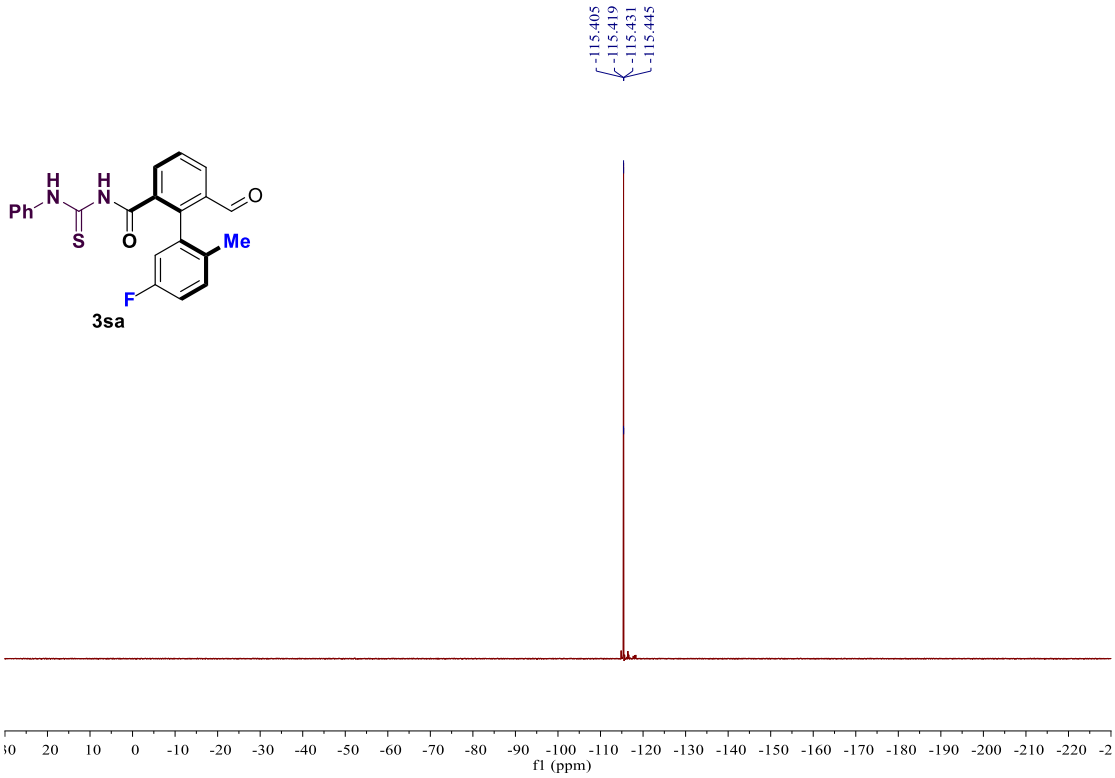
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ra.



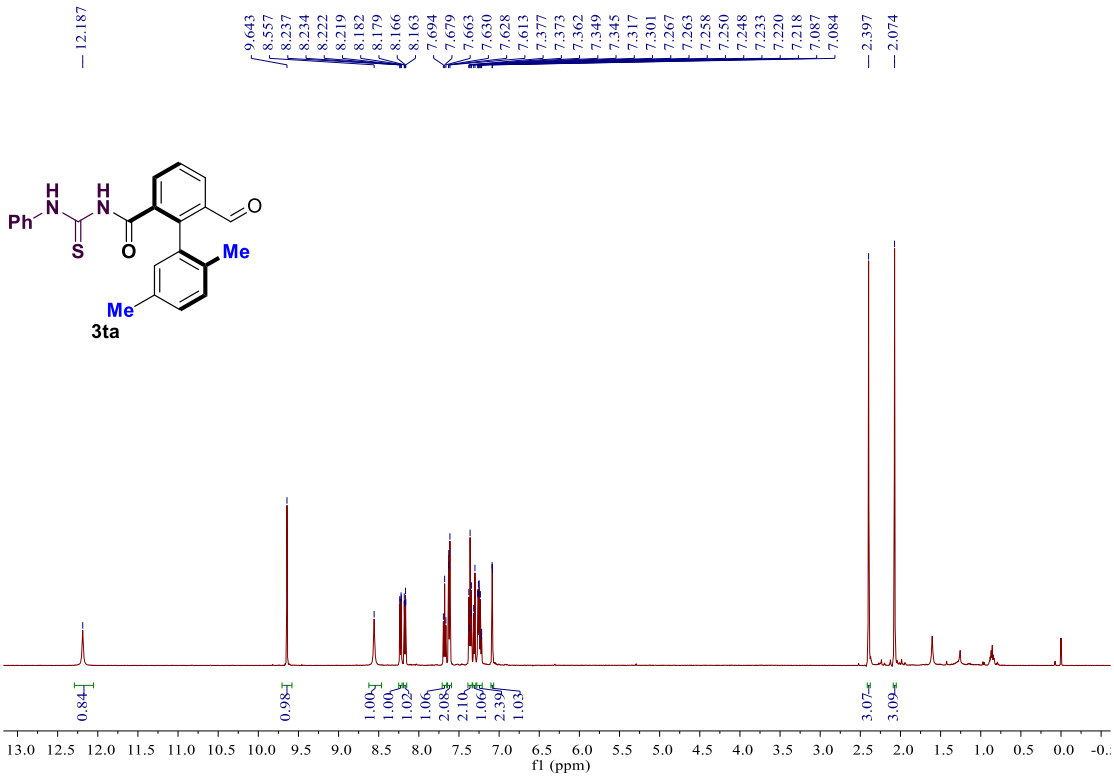
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3sa.



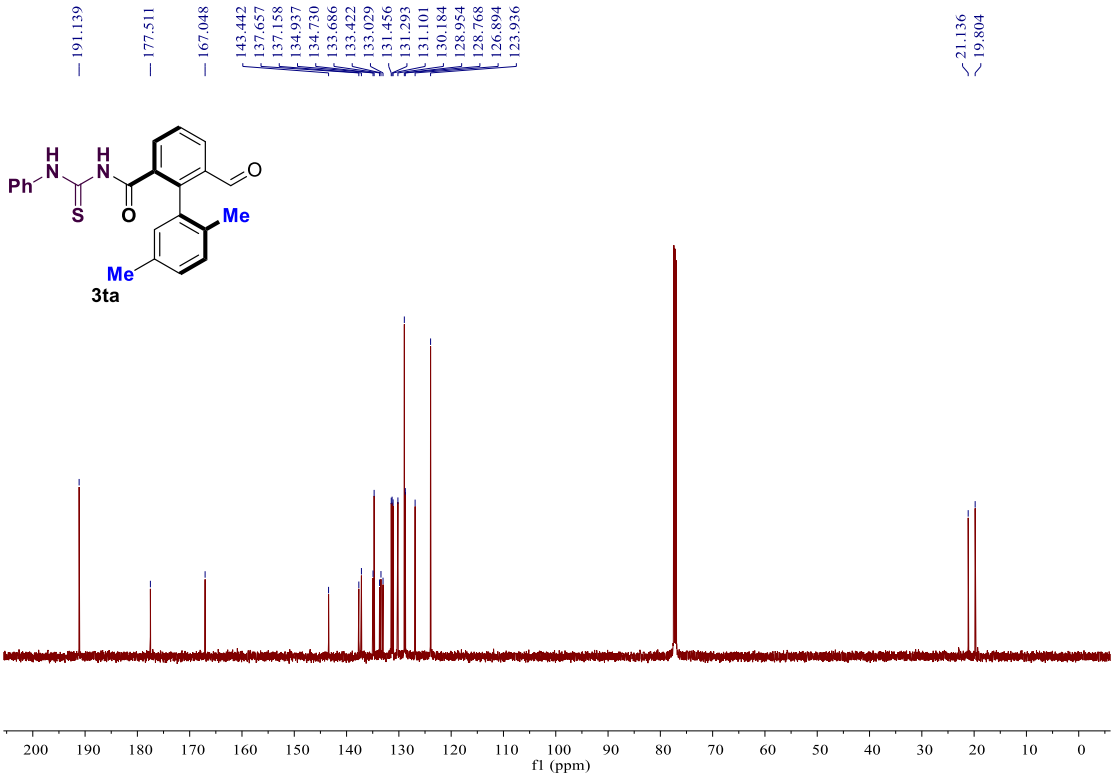
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3sa.



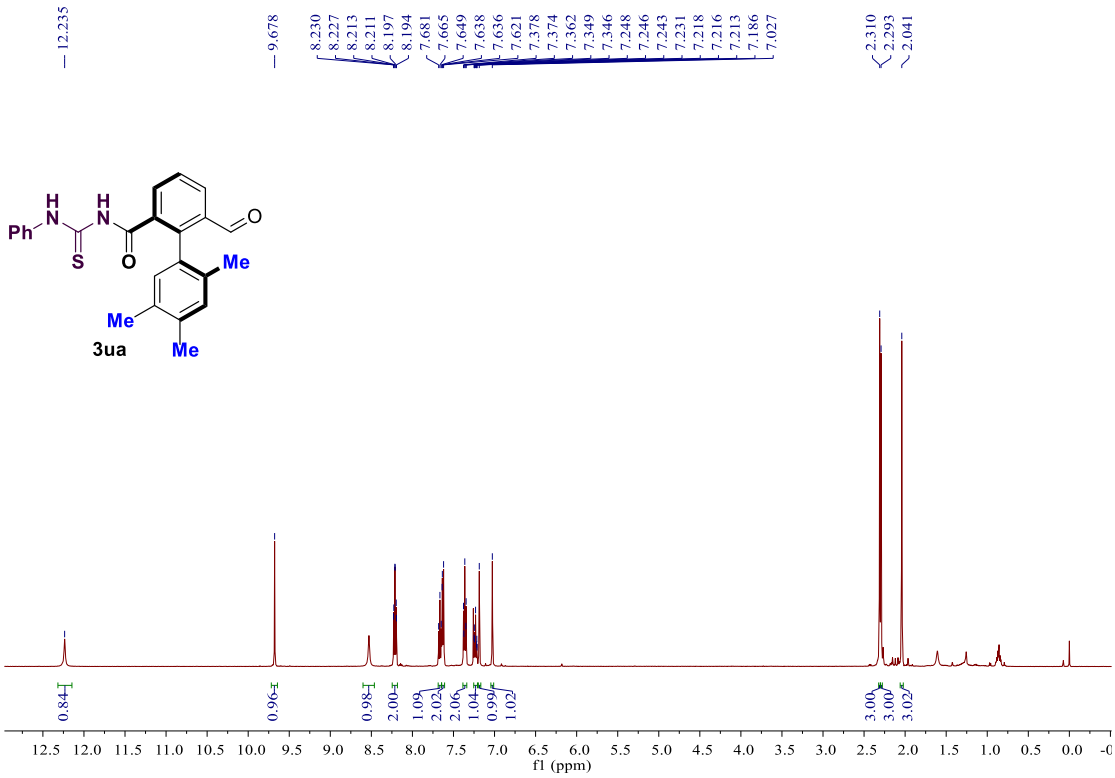
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3sa.



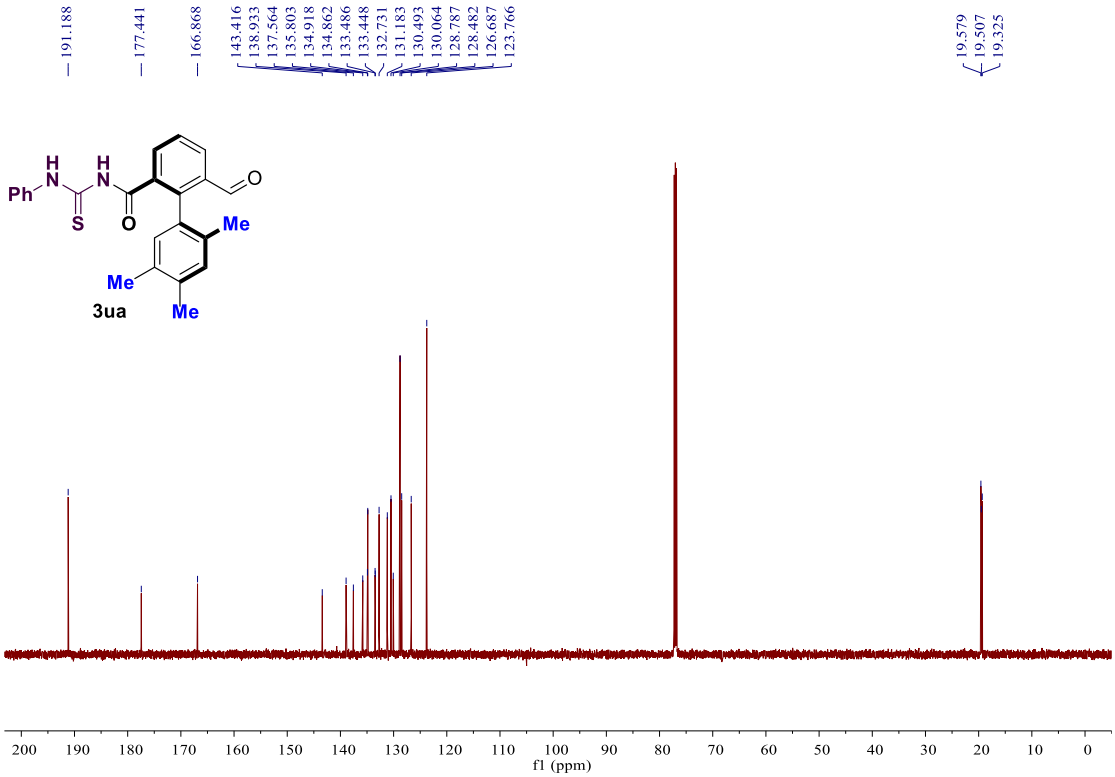
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ta.



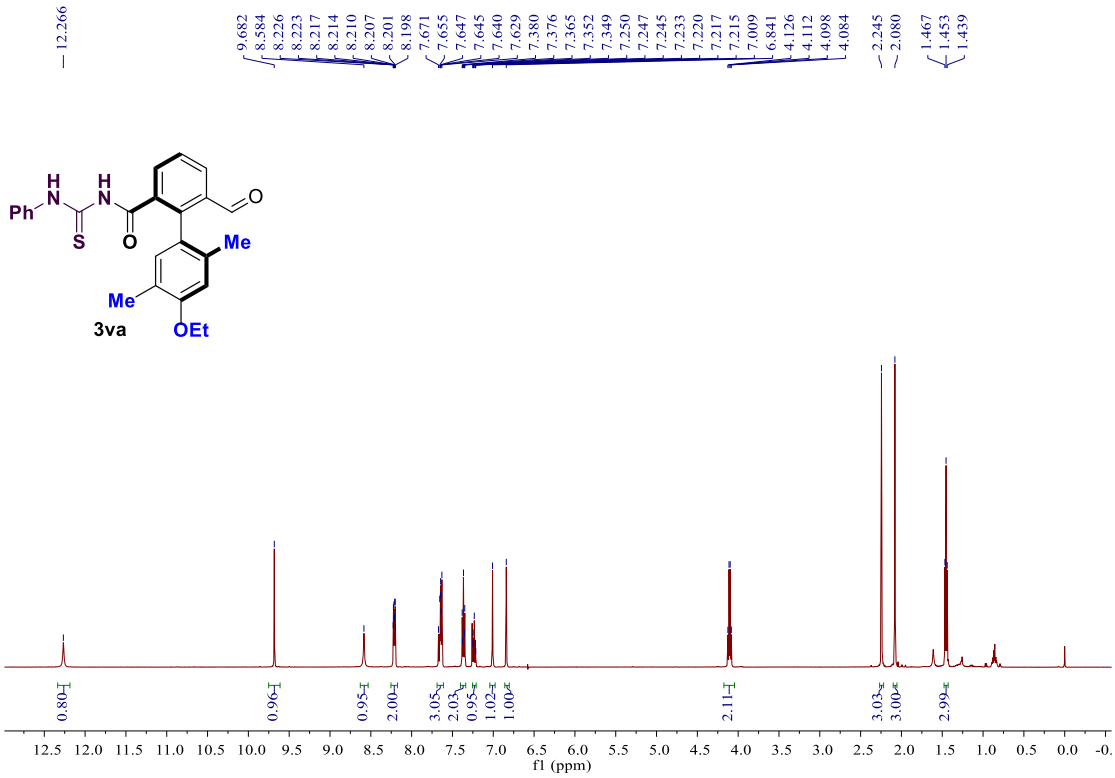
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ta.



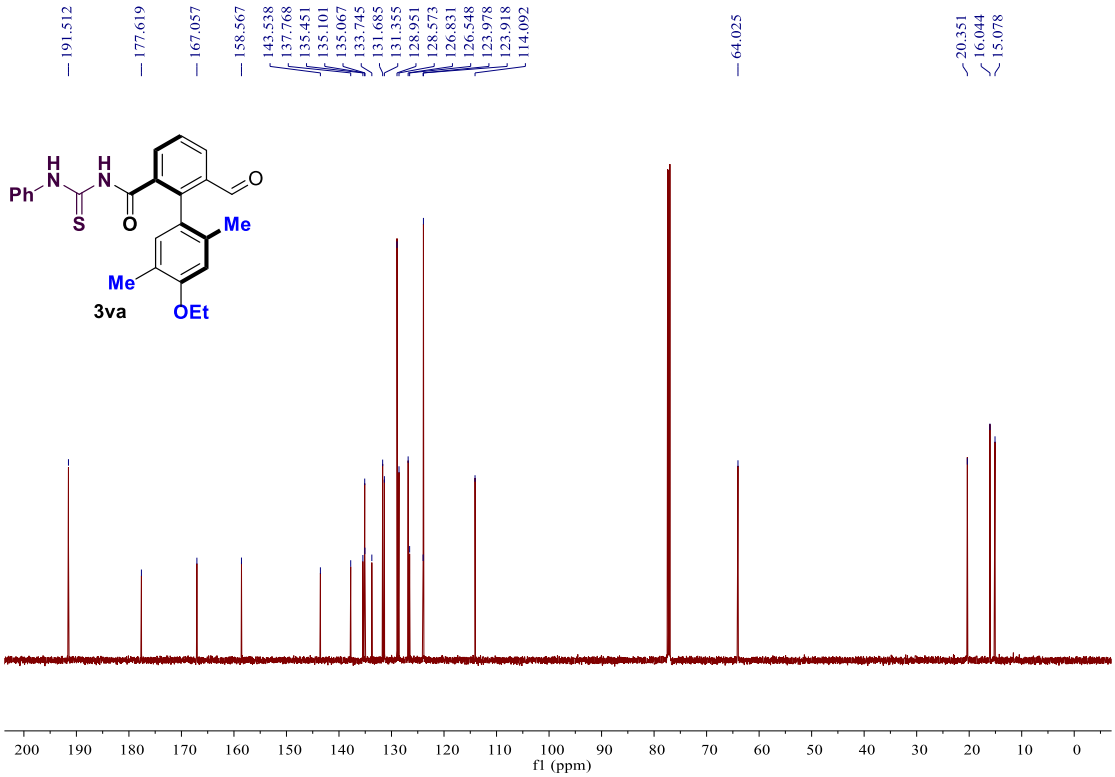
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ua.



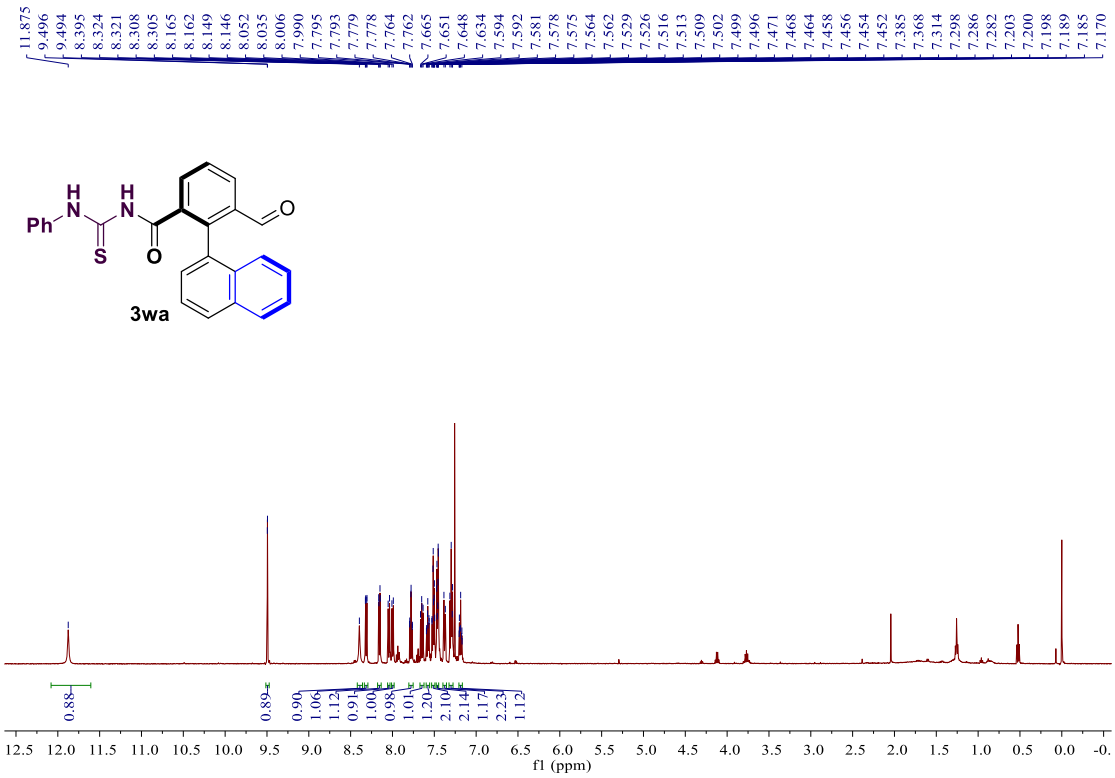
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ua.



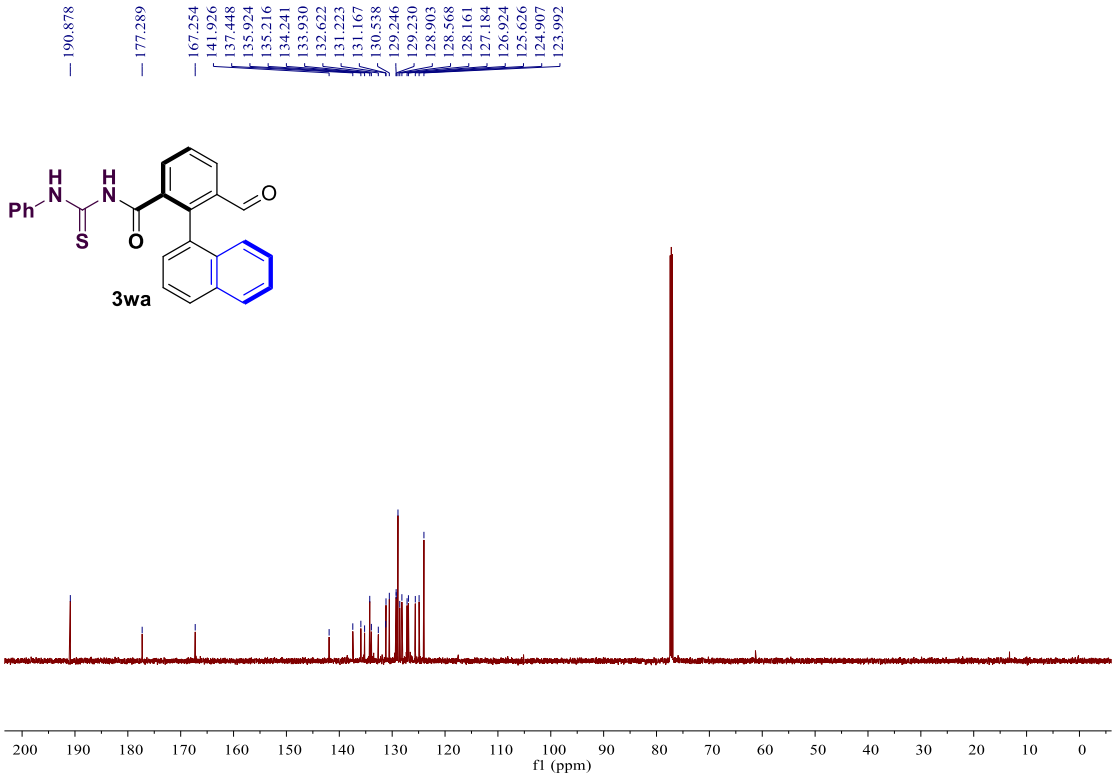
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3va.



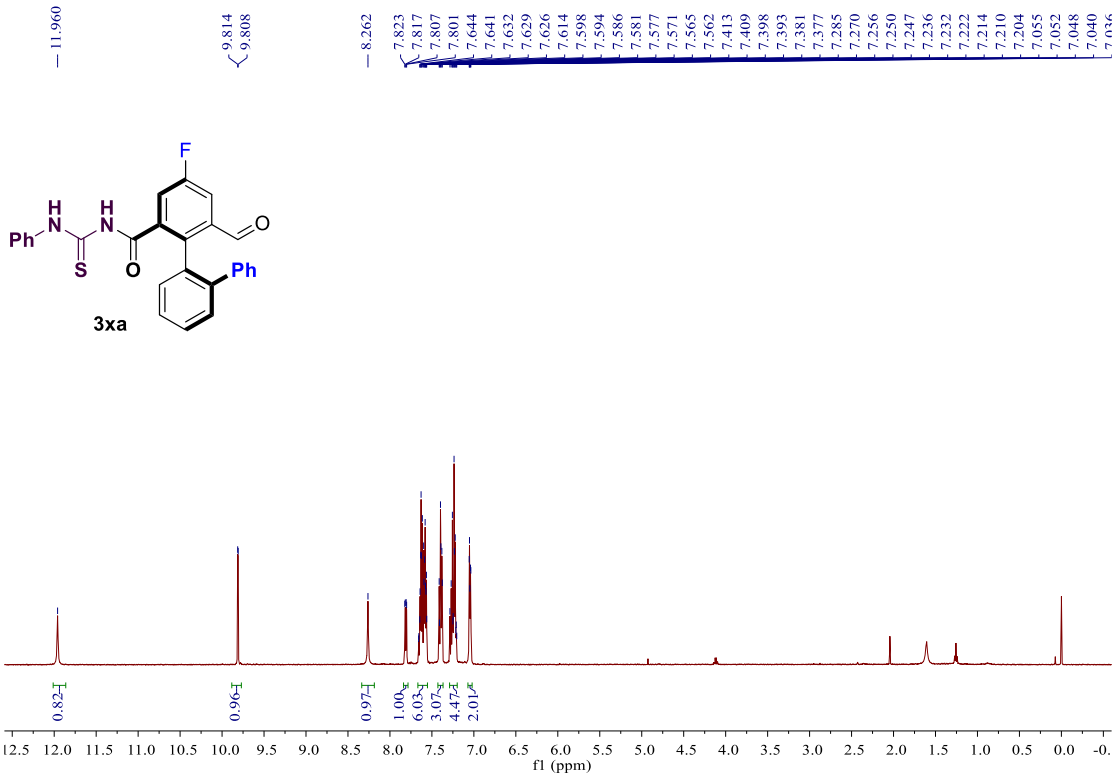
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3va.



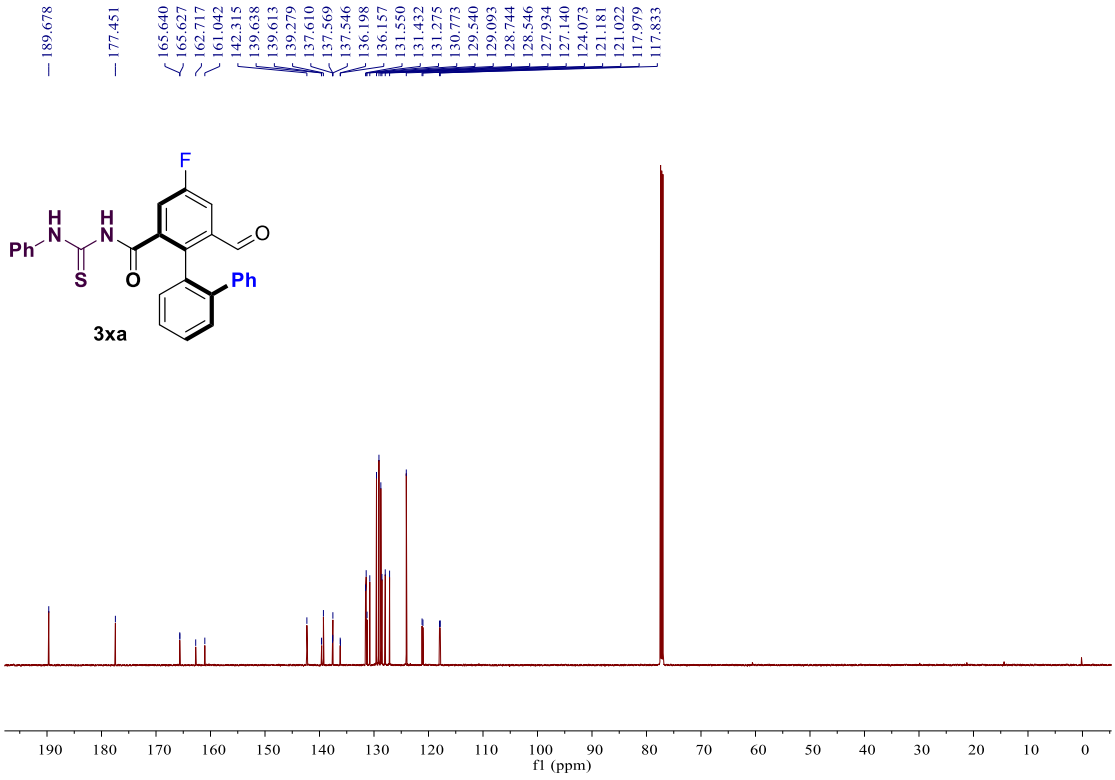
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3wa.



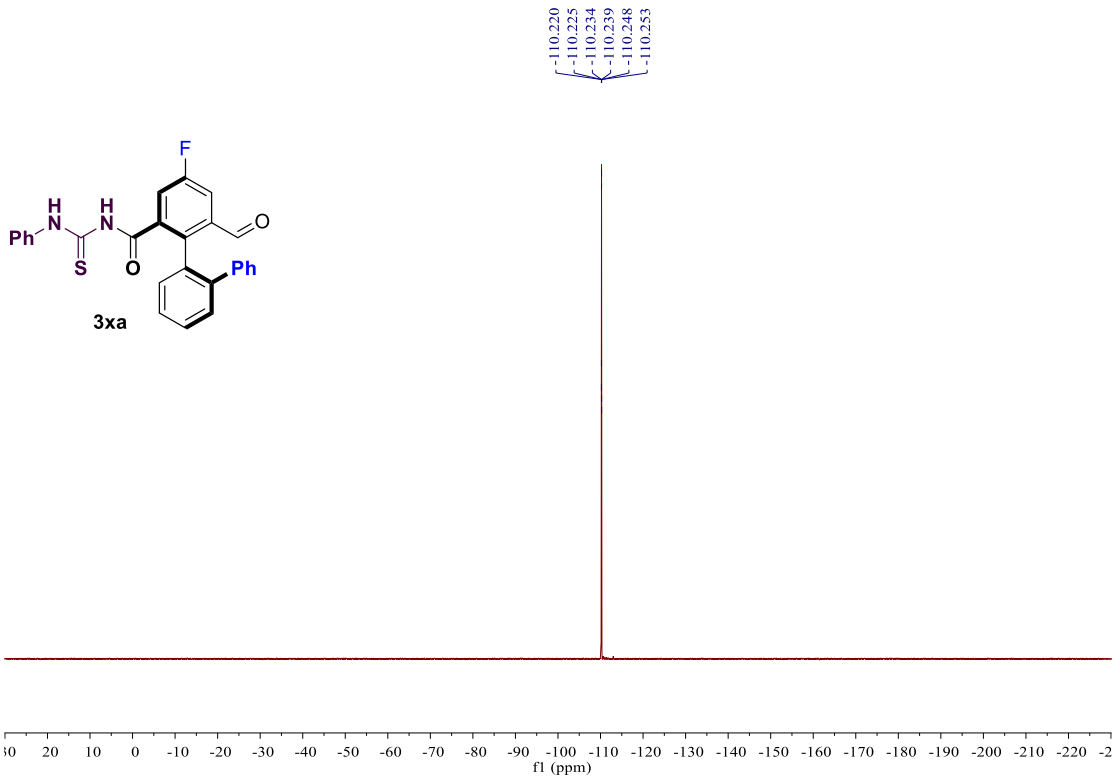
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3wa.



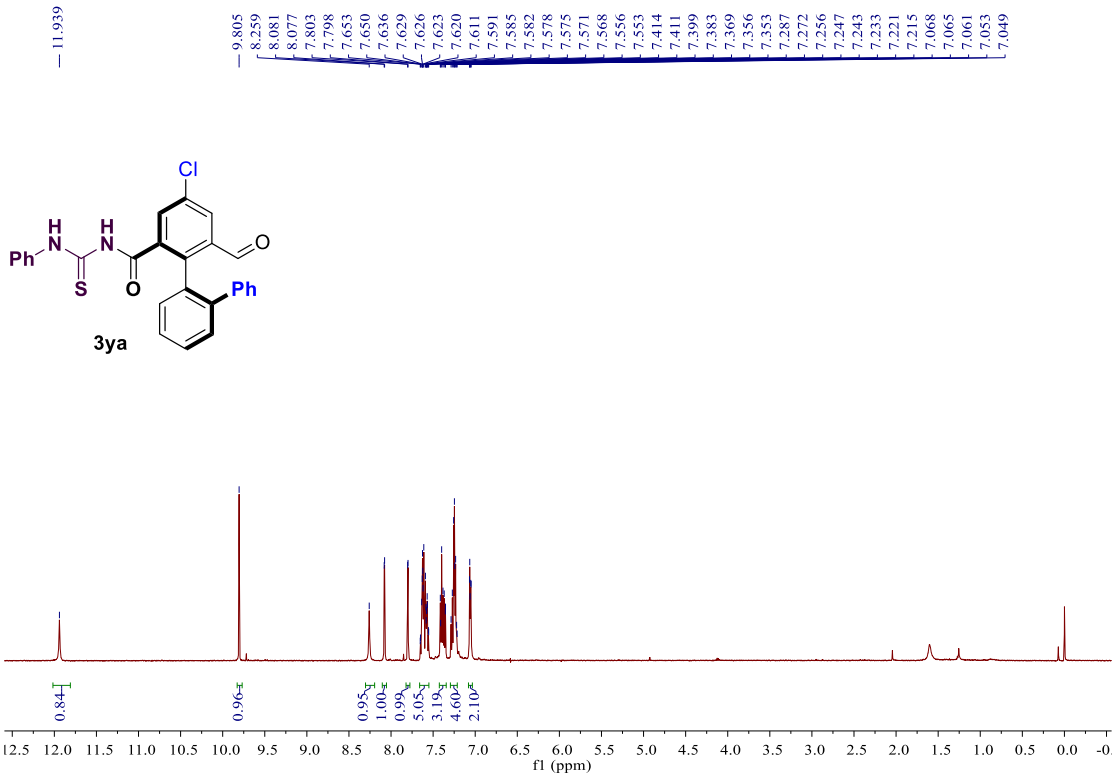
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3xa.



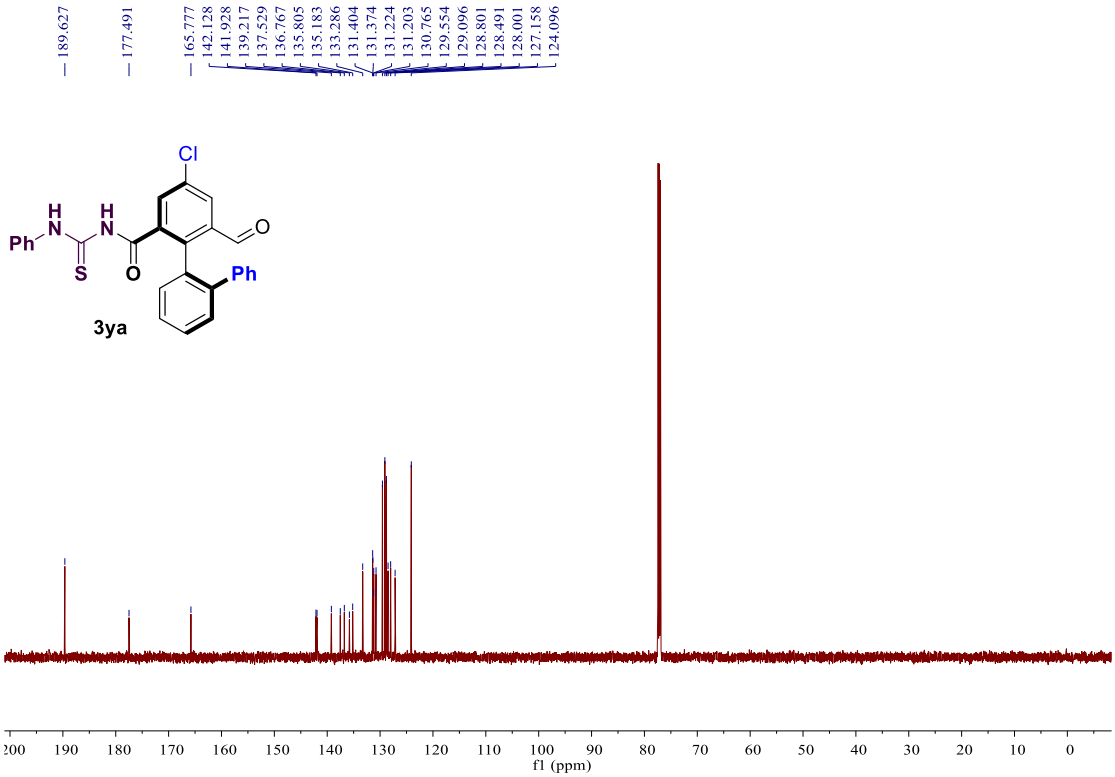
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3xa.



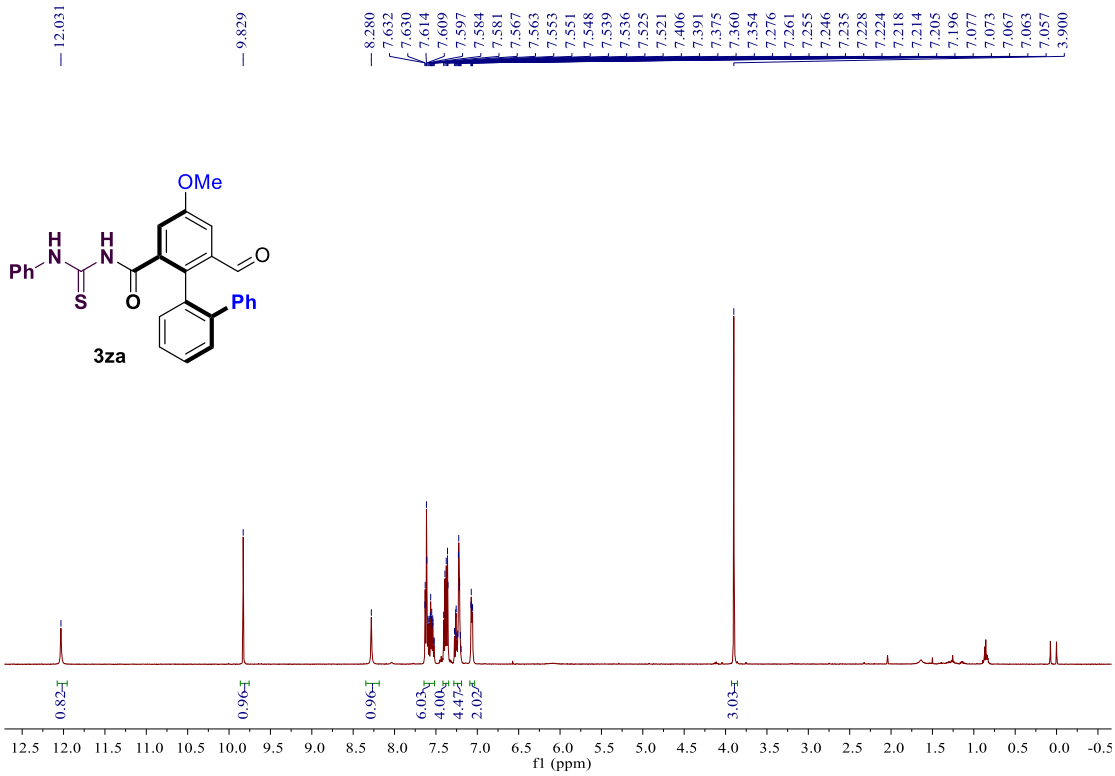
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3xa.



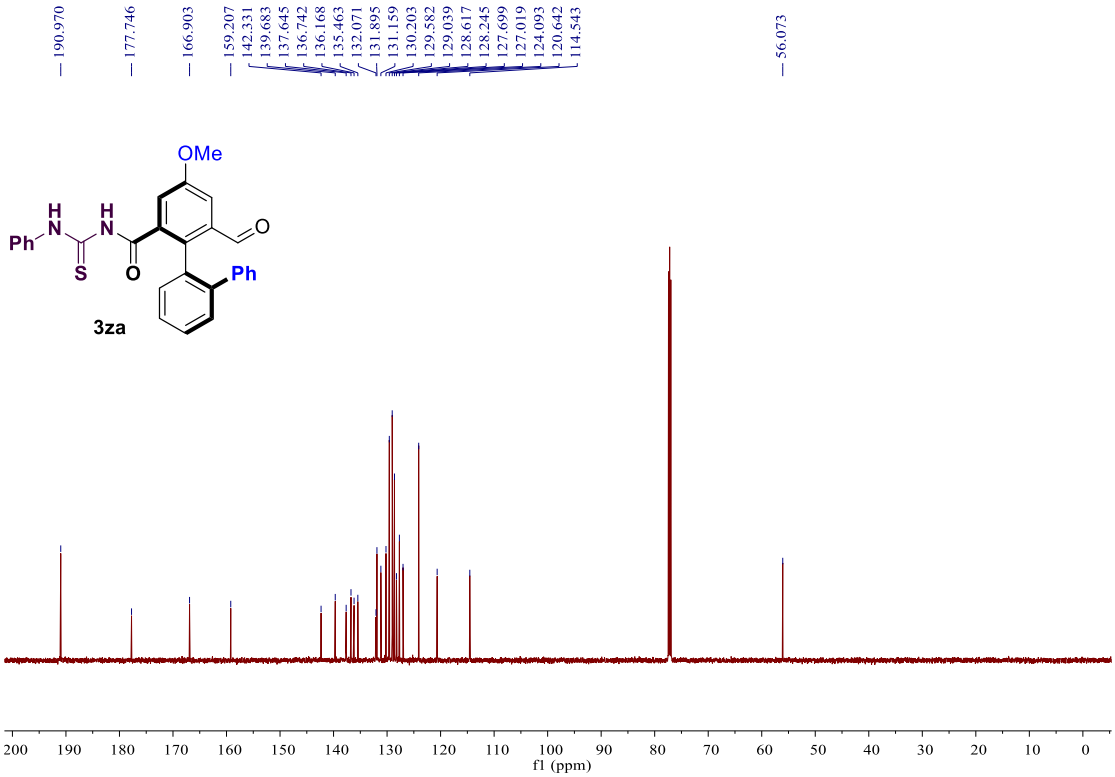
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ya.



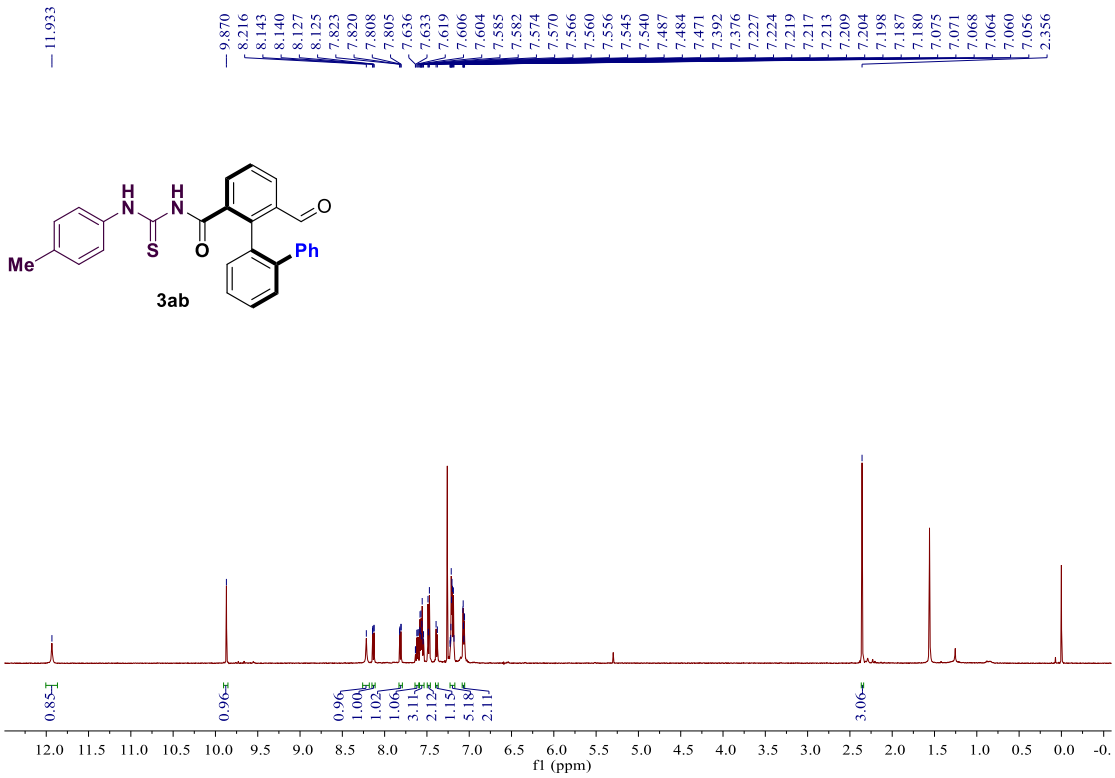
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ya.



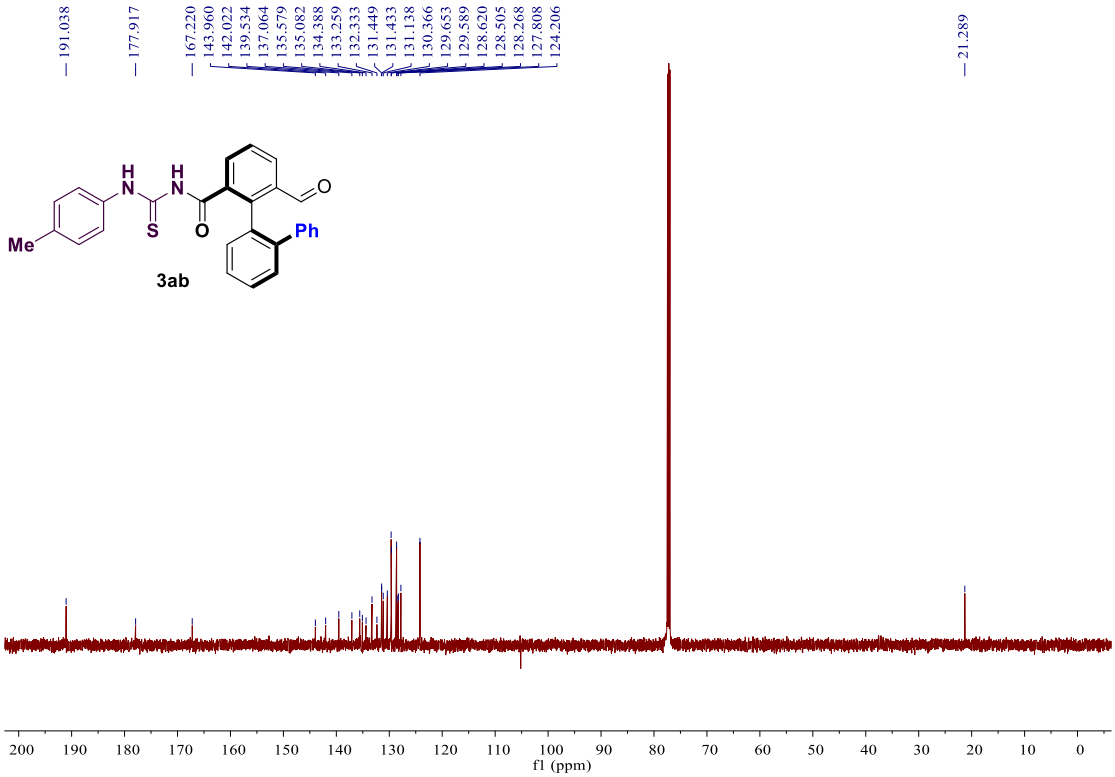
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3za.



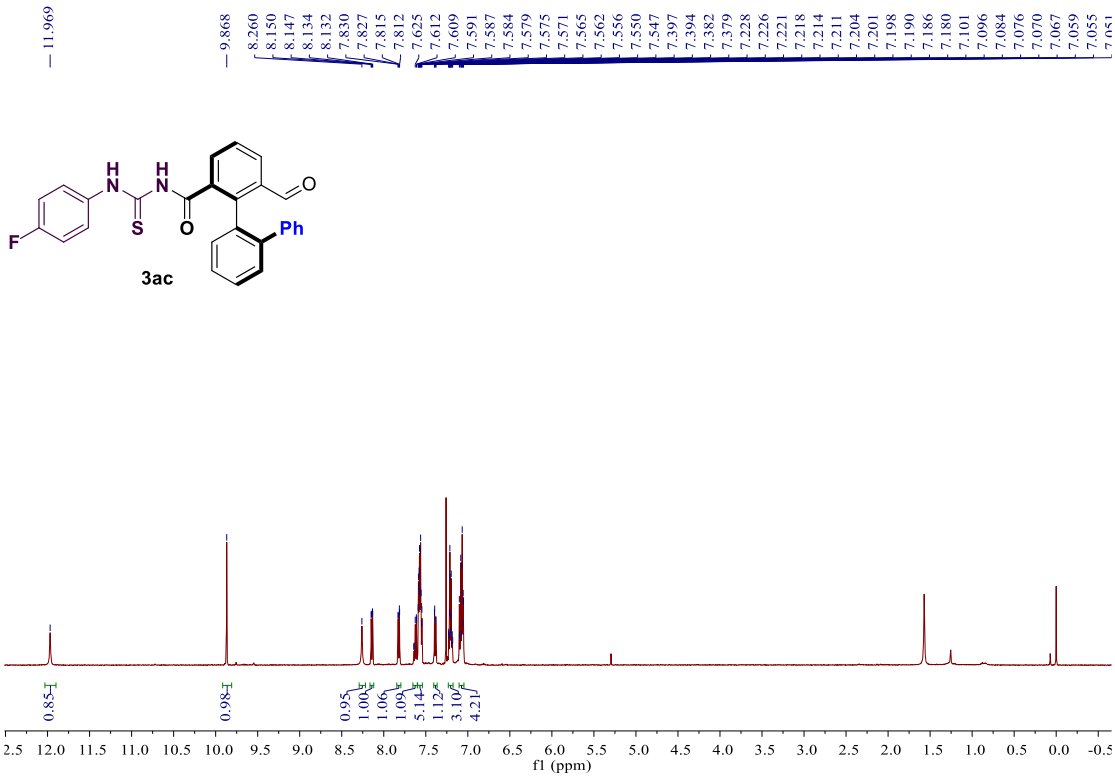
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3za.



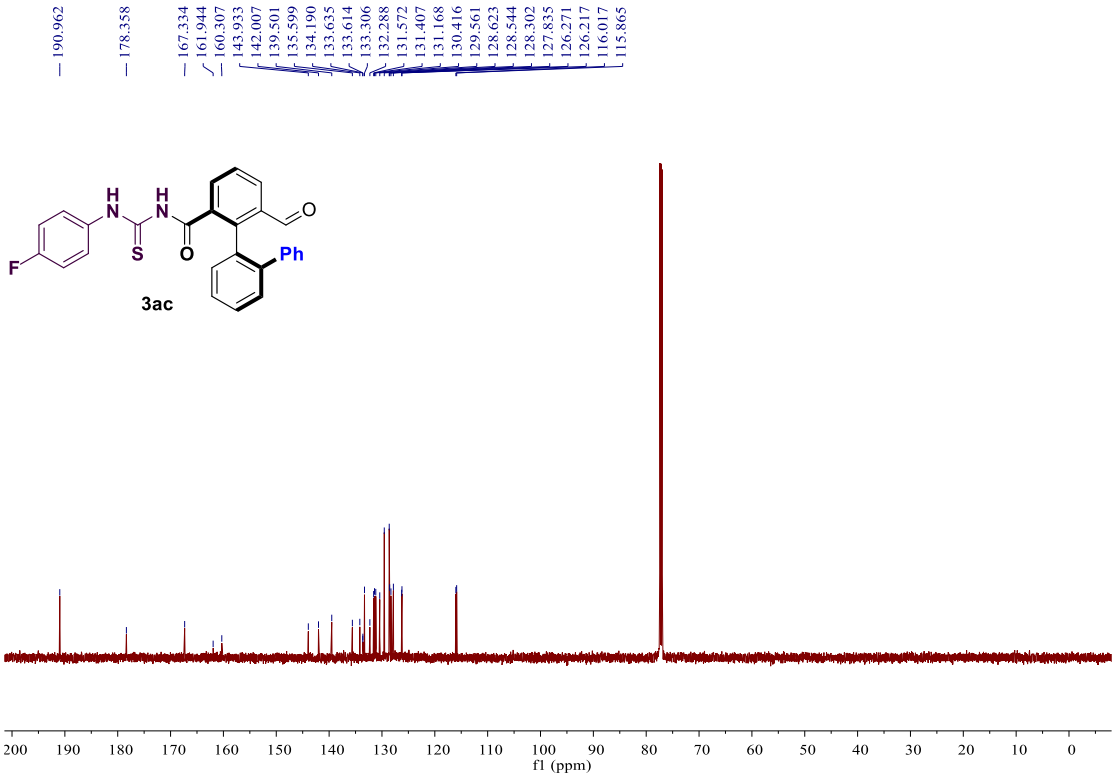
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ab.



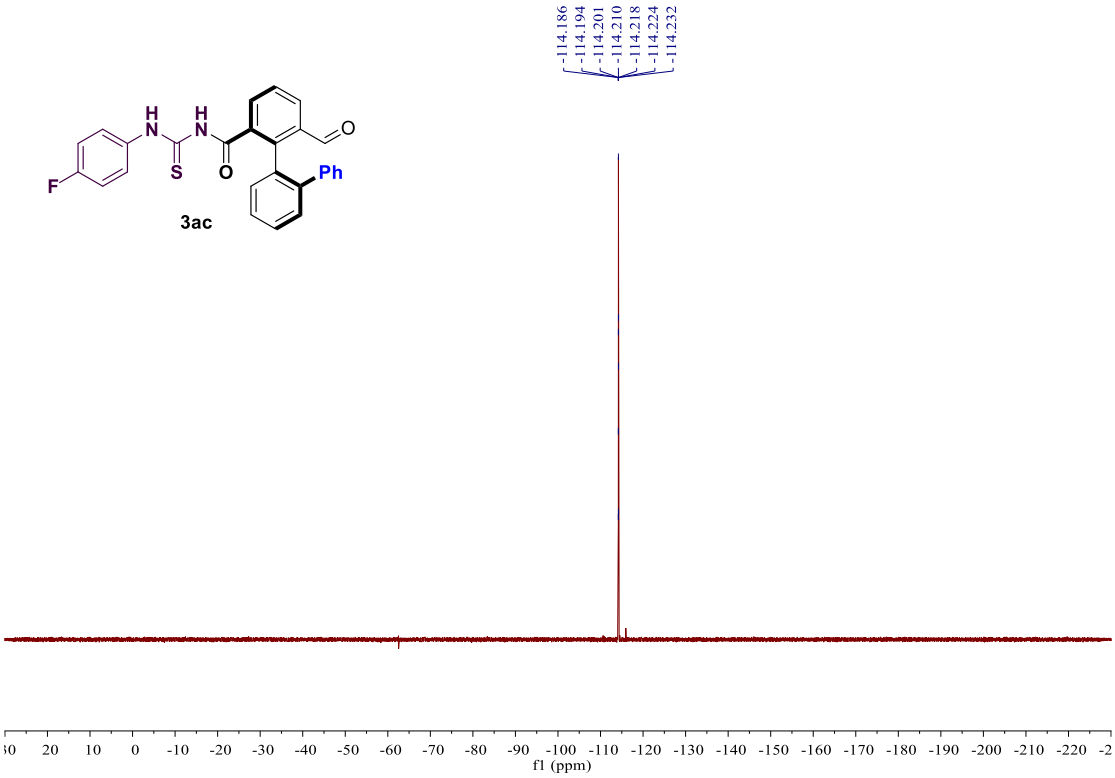
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ab.



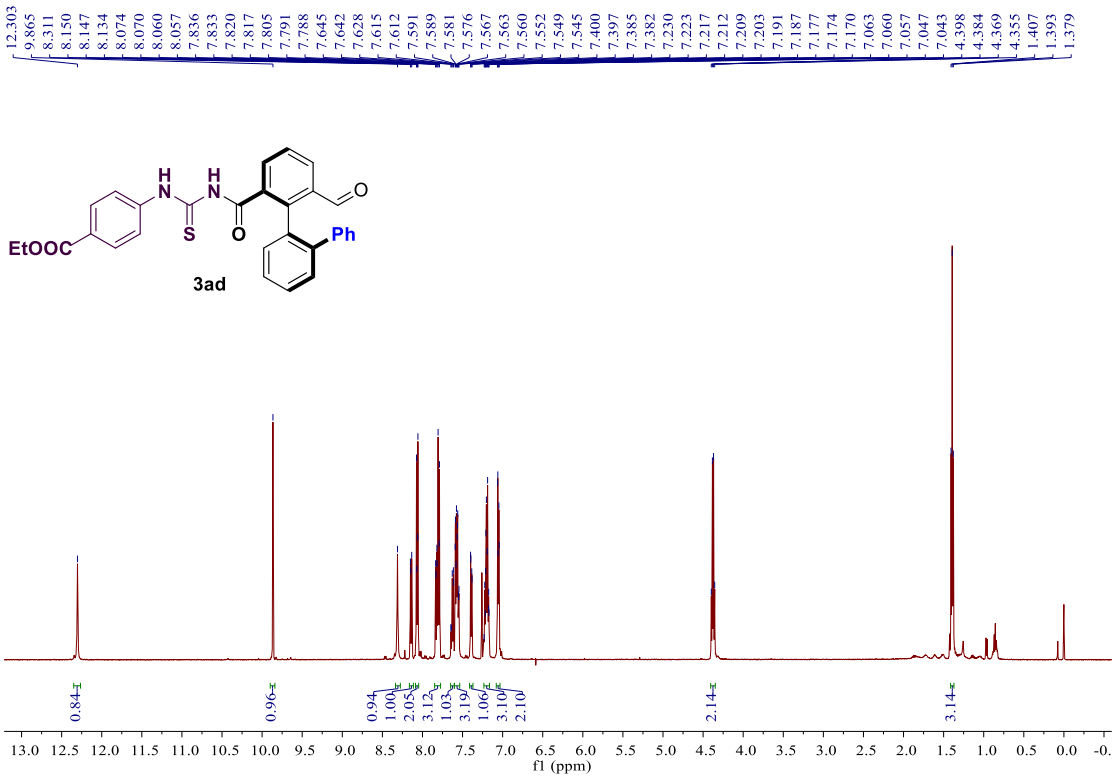
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ac.



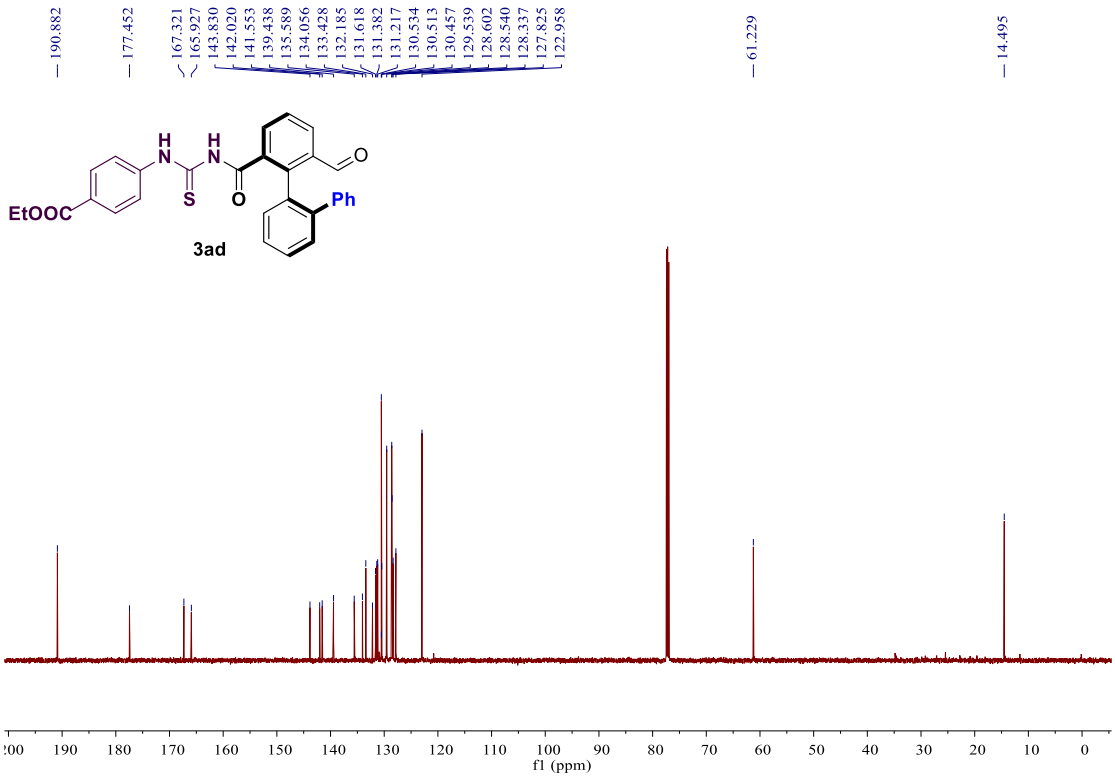
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ac.



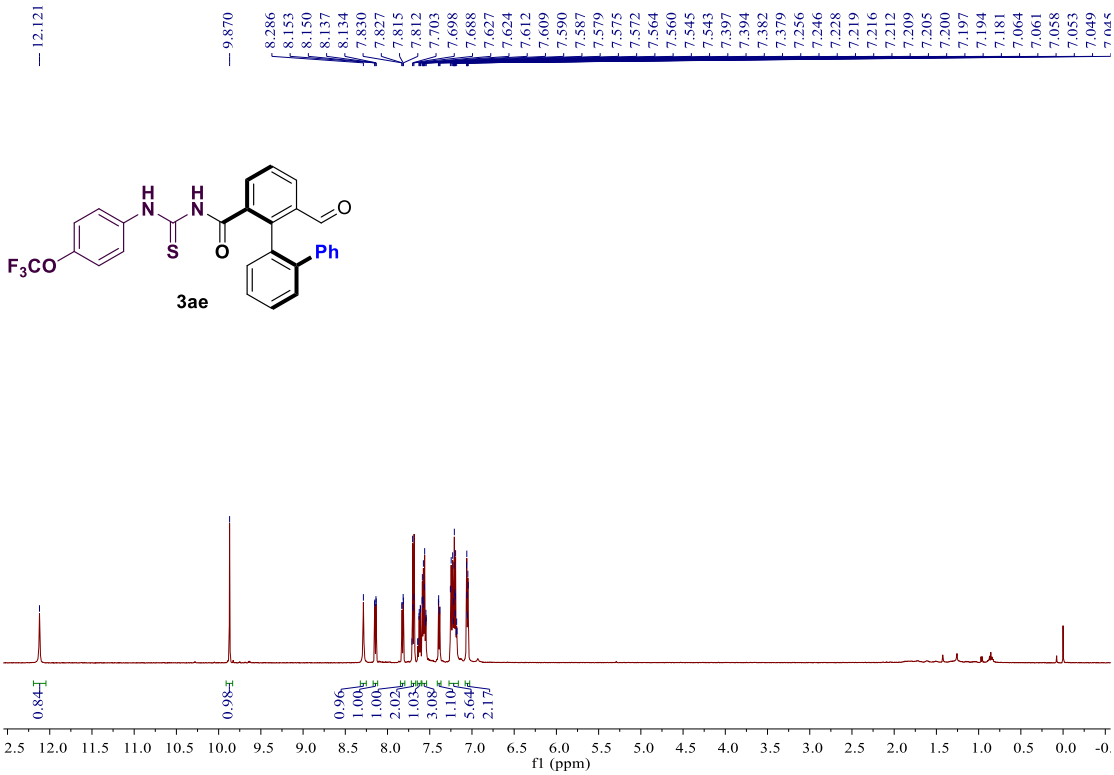
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3ac.



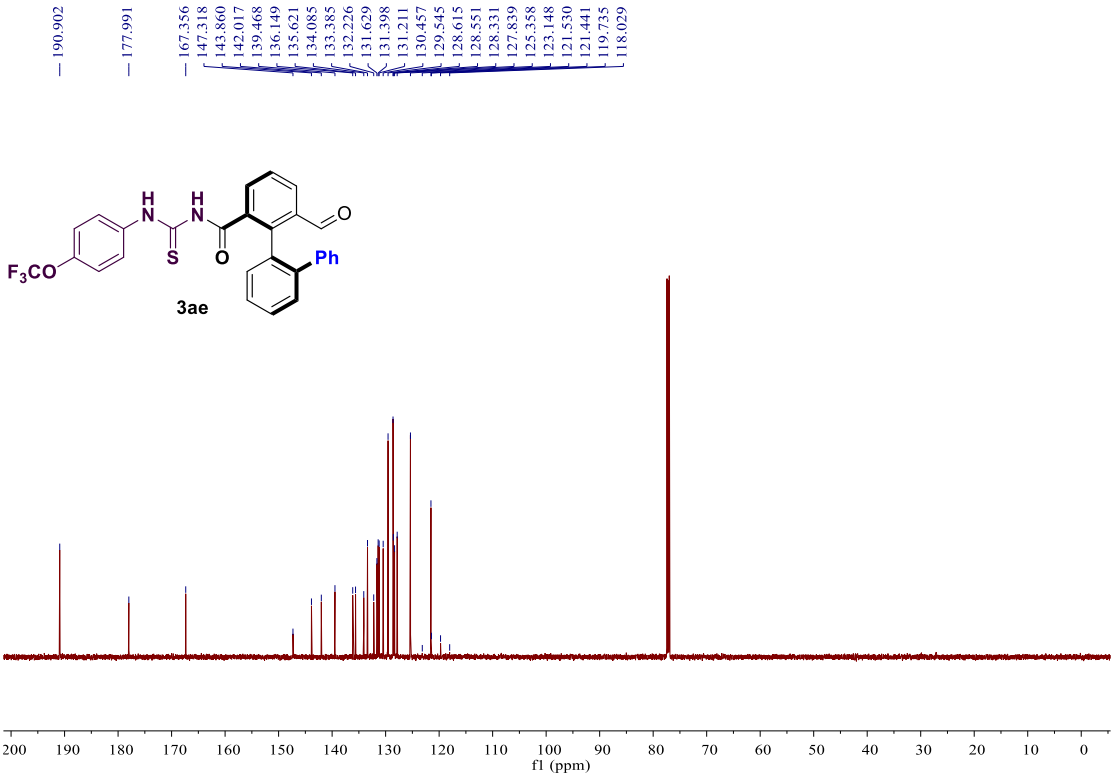
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ad.



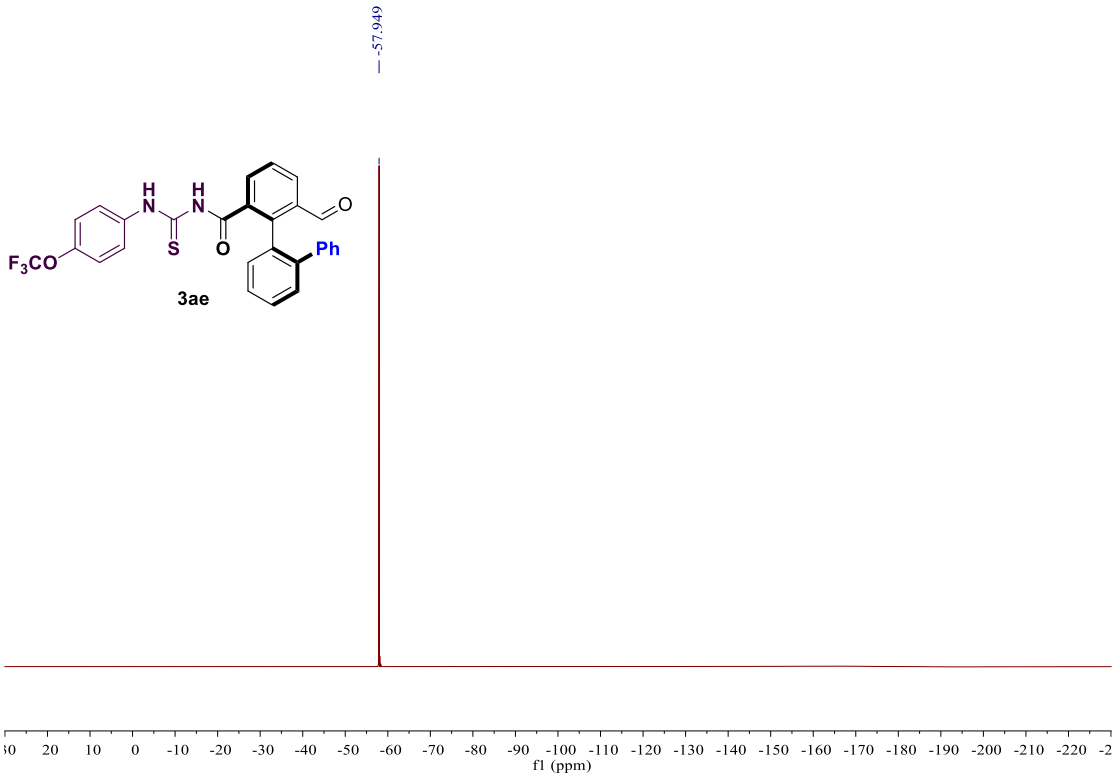
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ad.



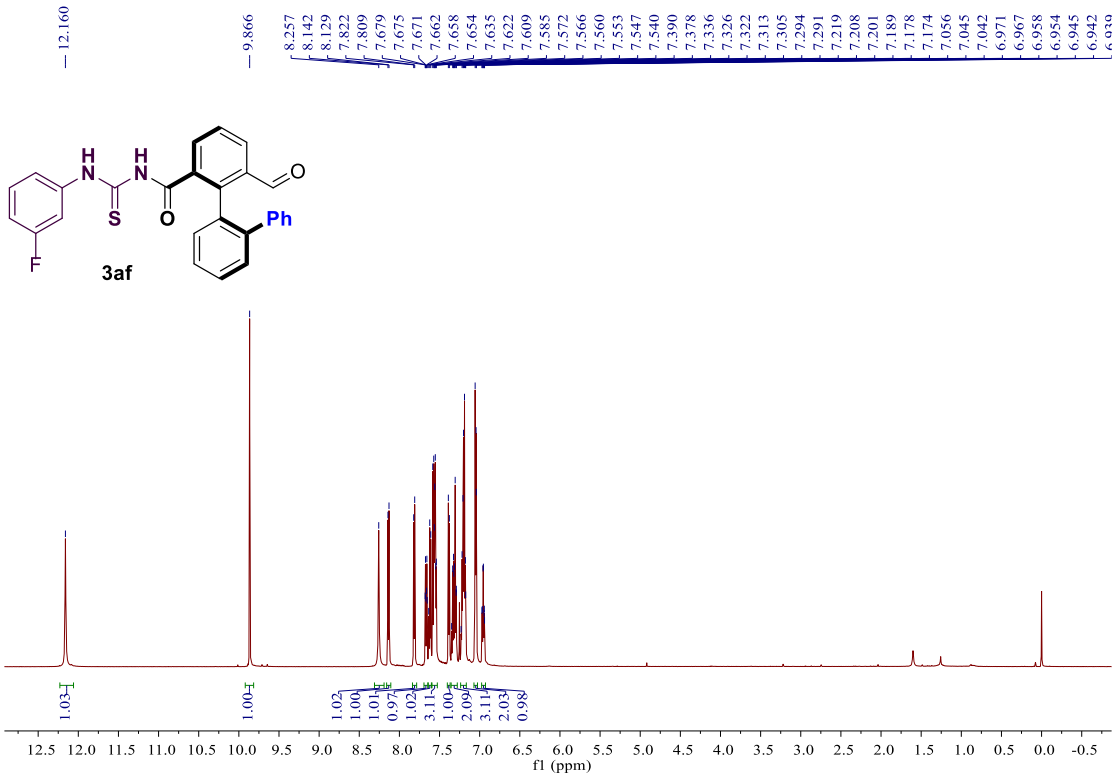
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ae.



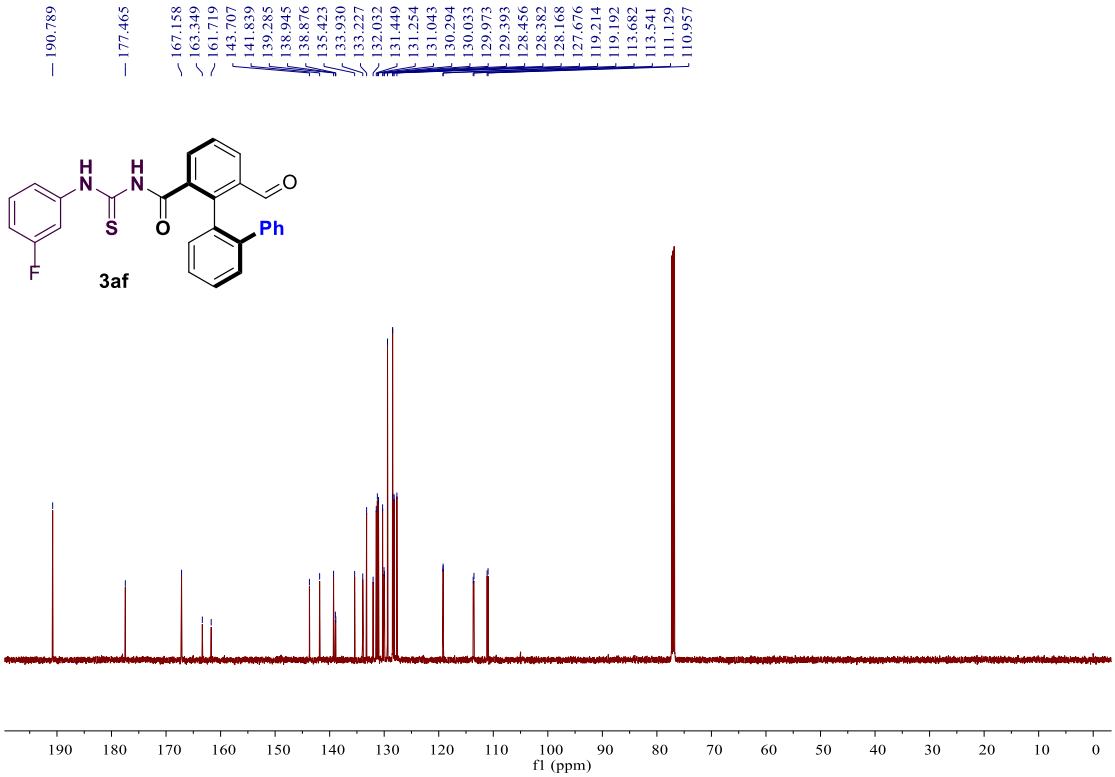
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ae.



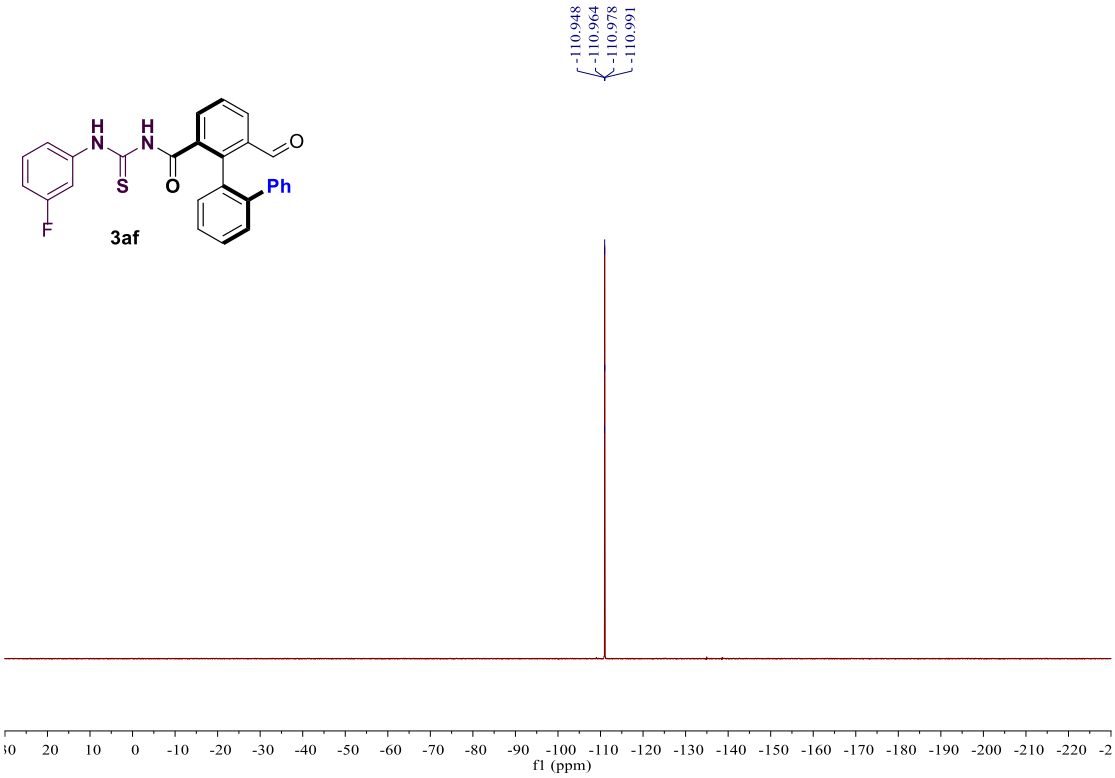
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3ae.



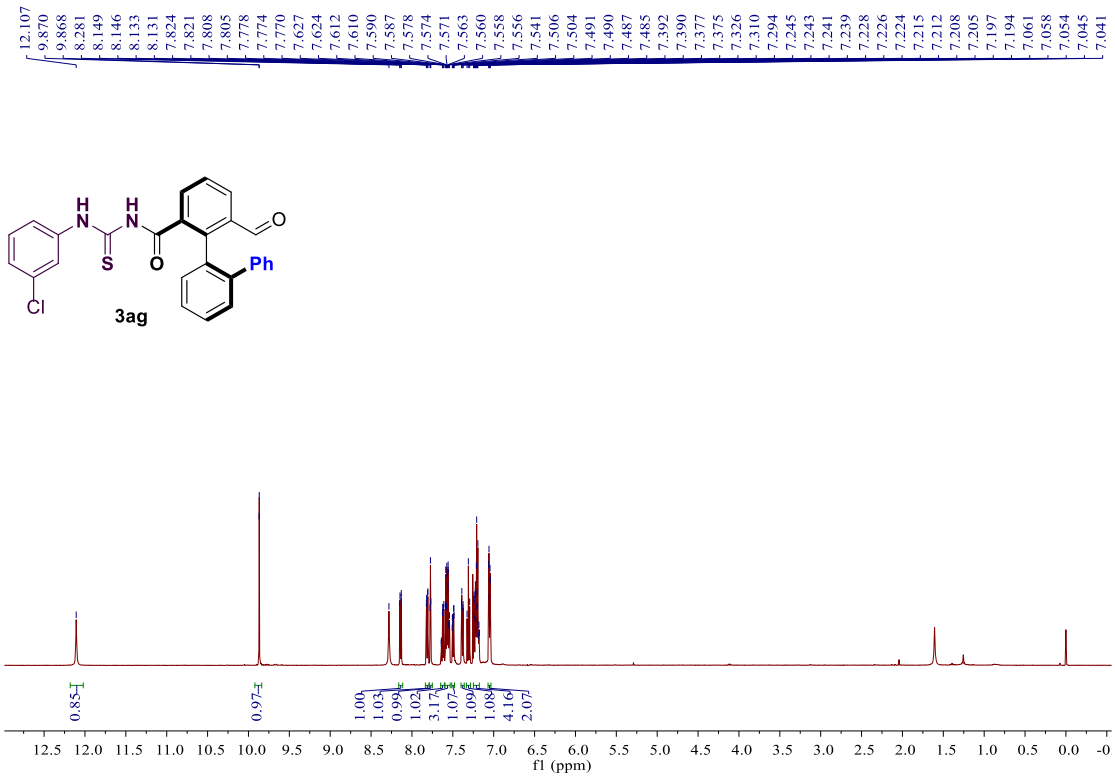
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3af.



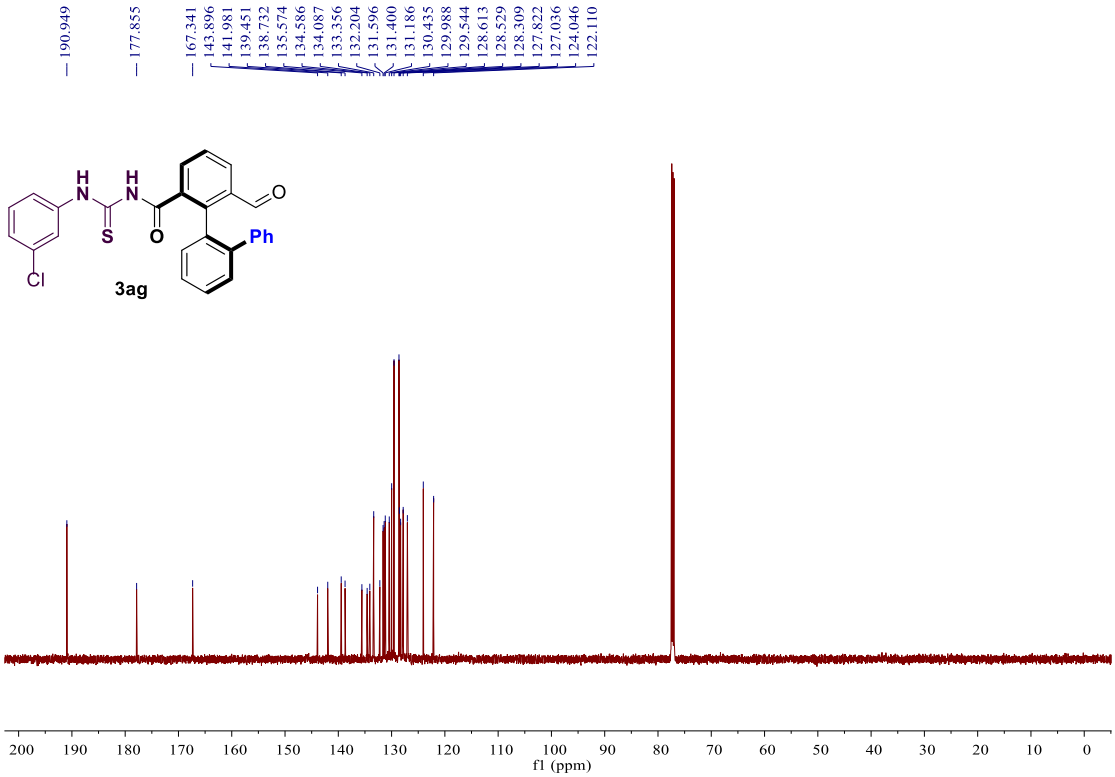
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3af.



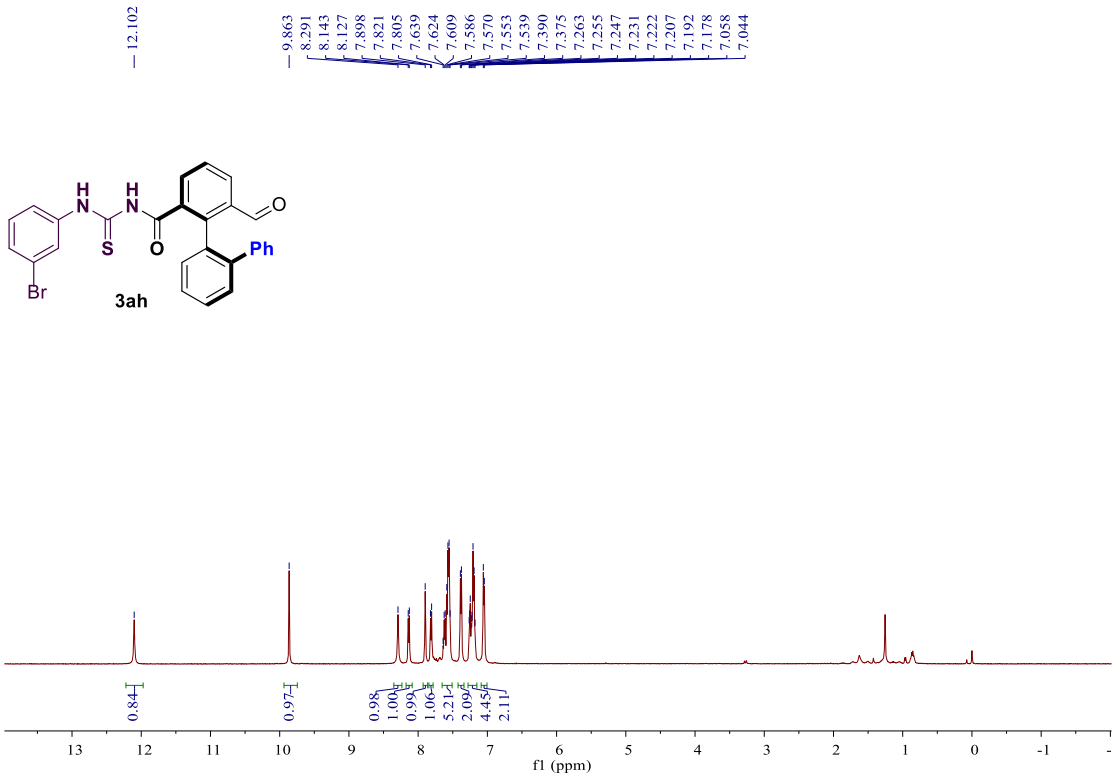
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3af.



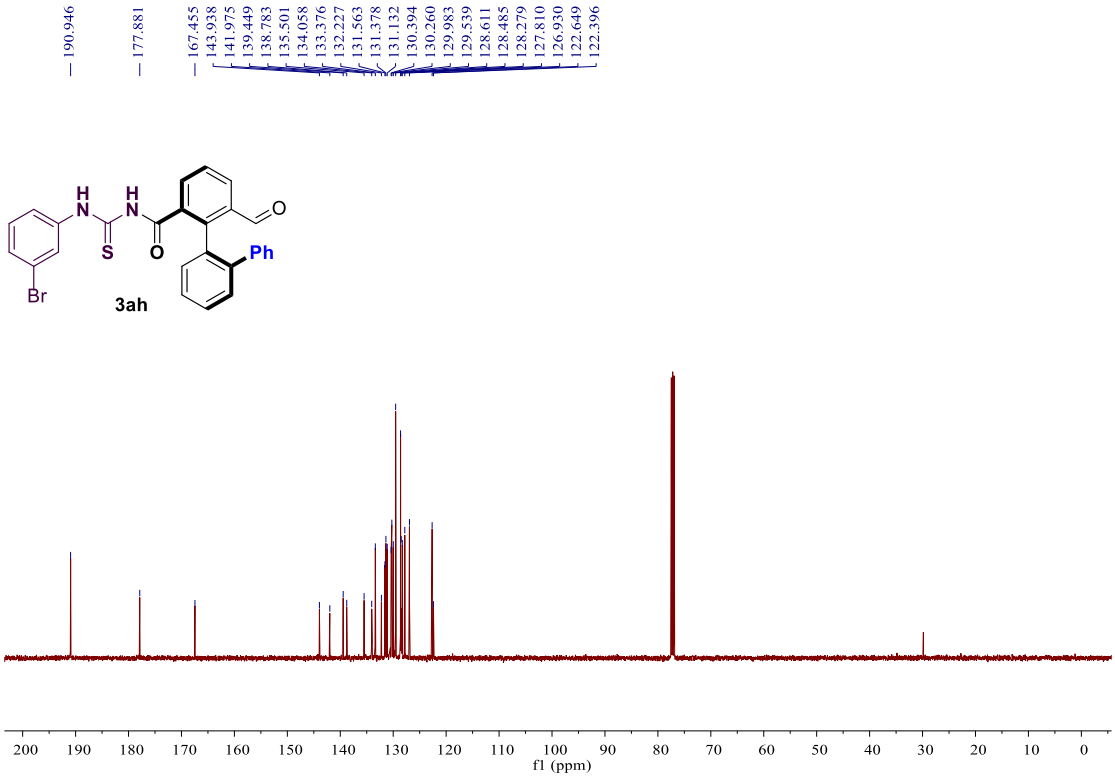
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ag.



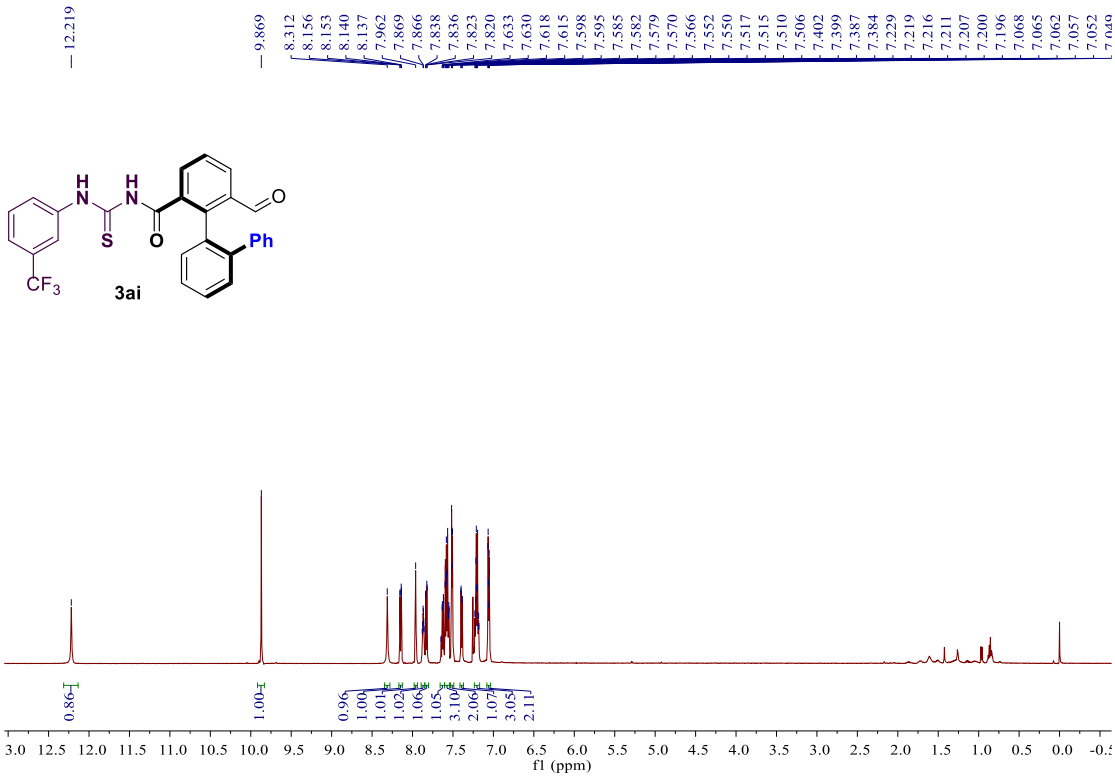
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ag.



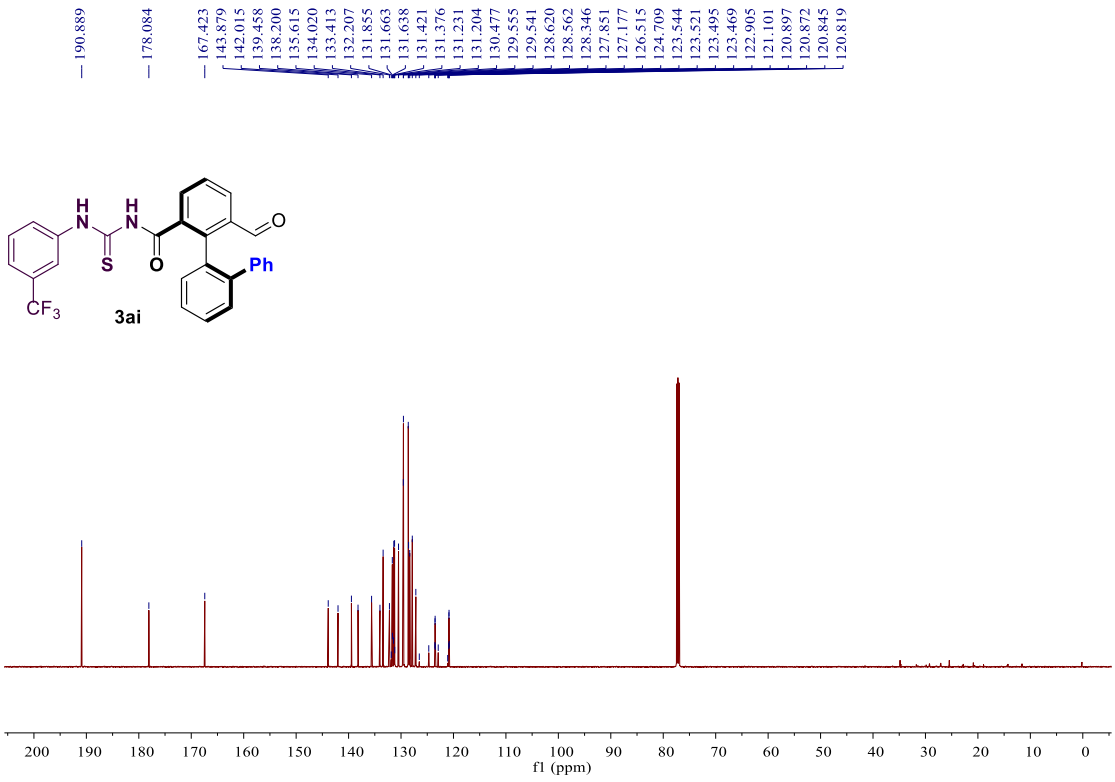
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ah.



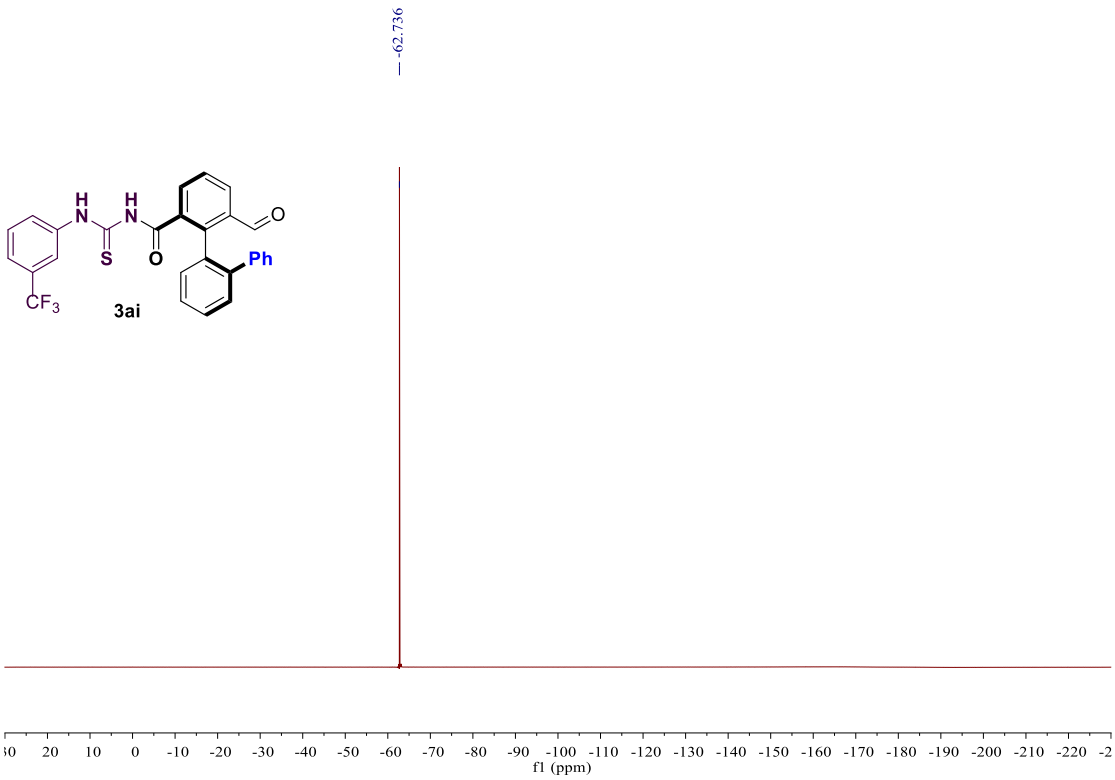
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ah.



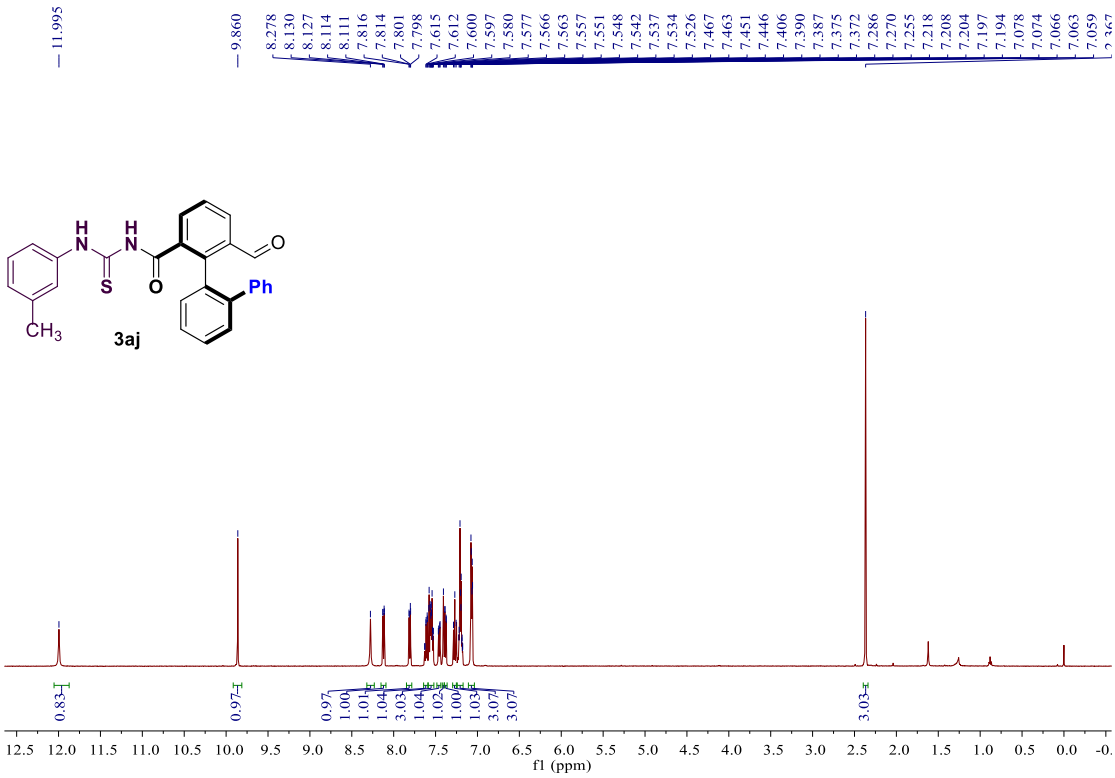
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ai.



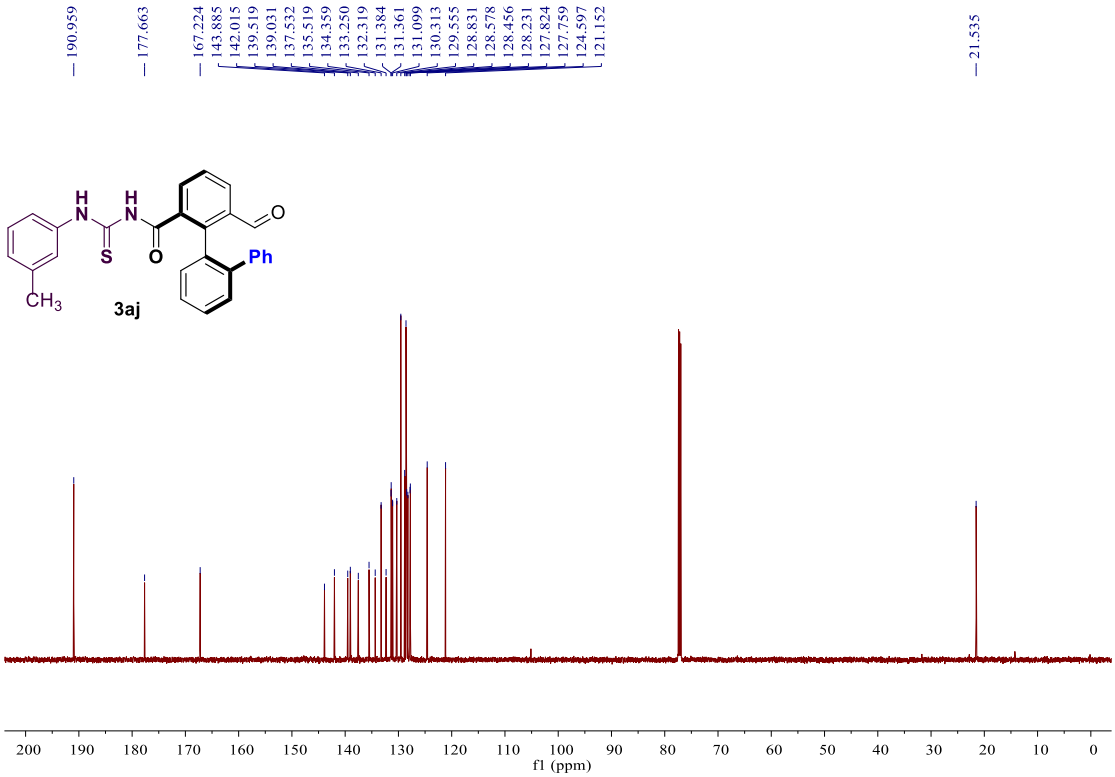
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ai.



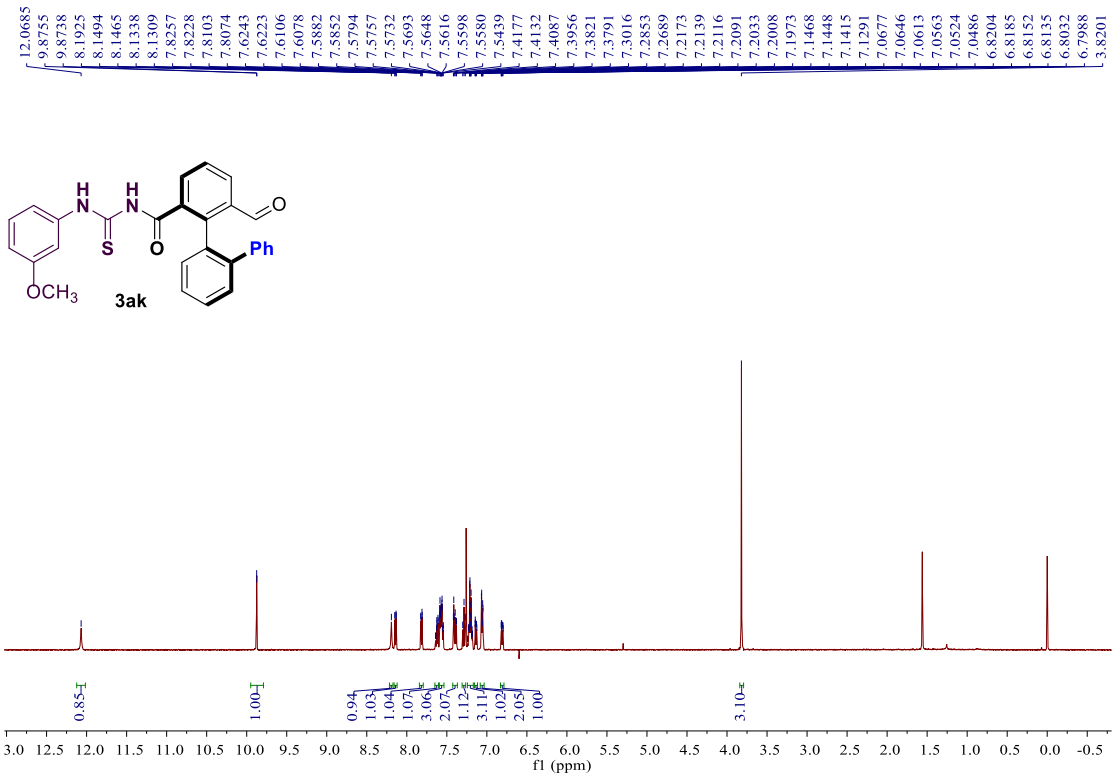
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3ai.



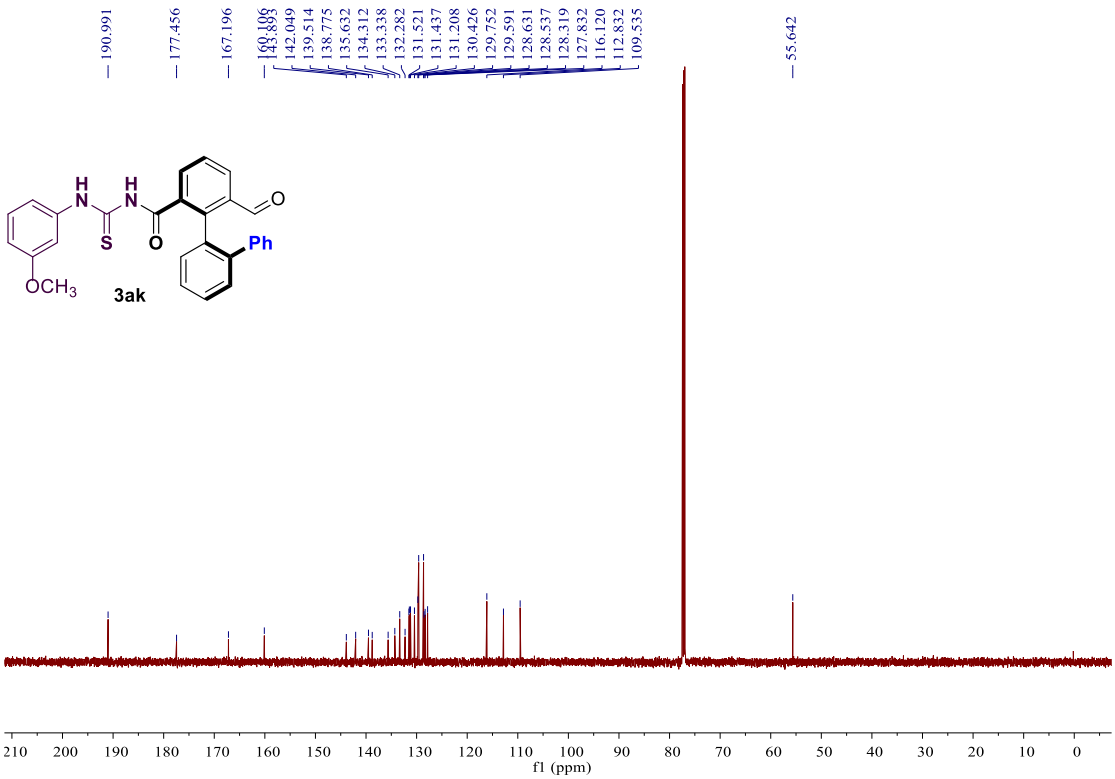
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aj.



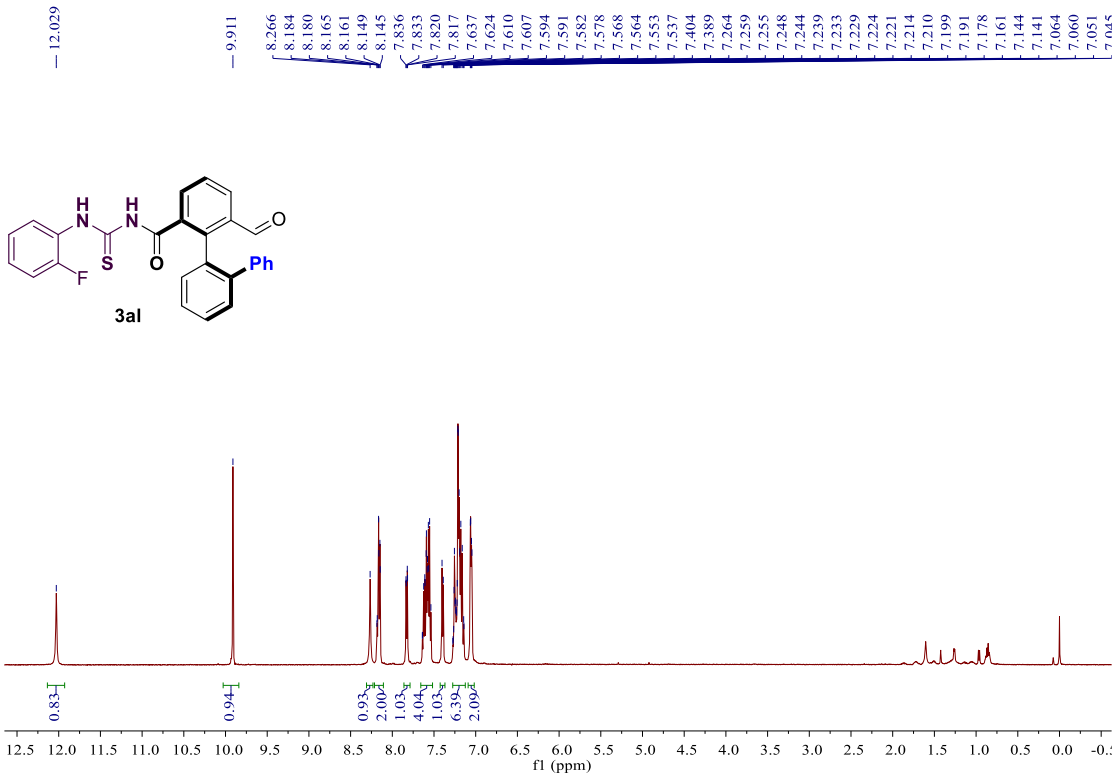
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3aj.



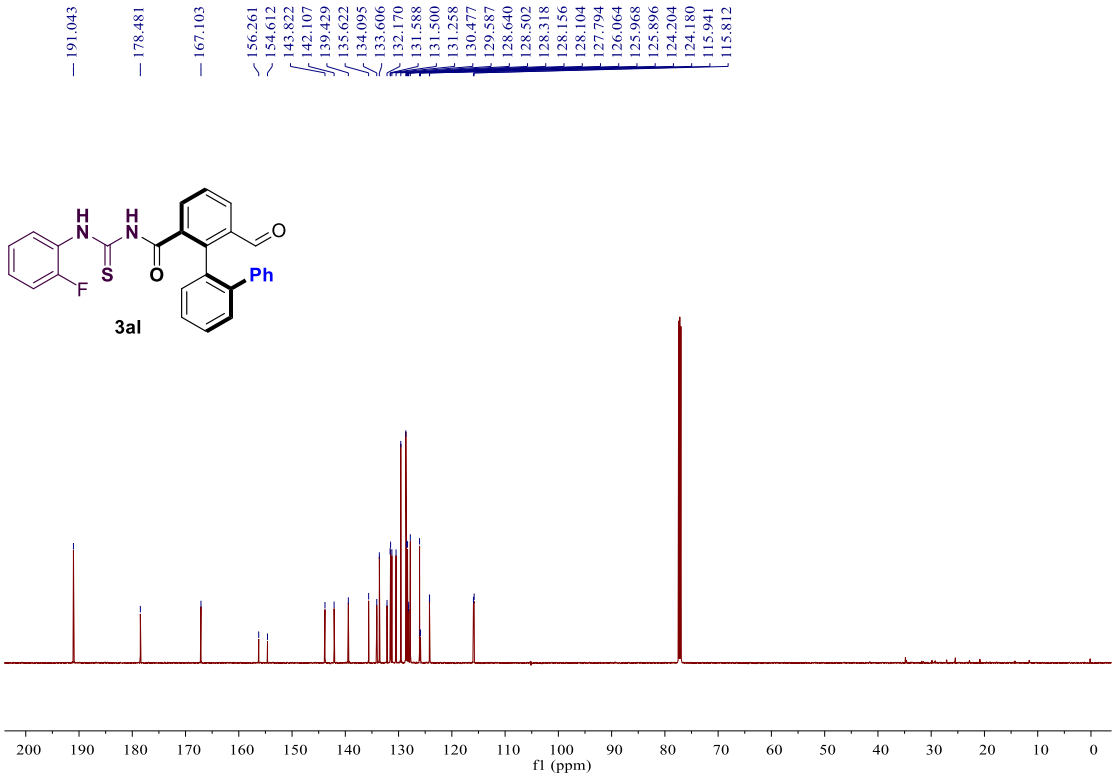
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ak.



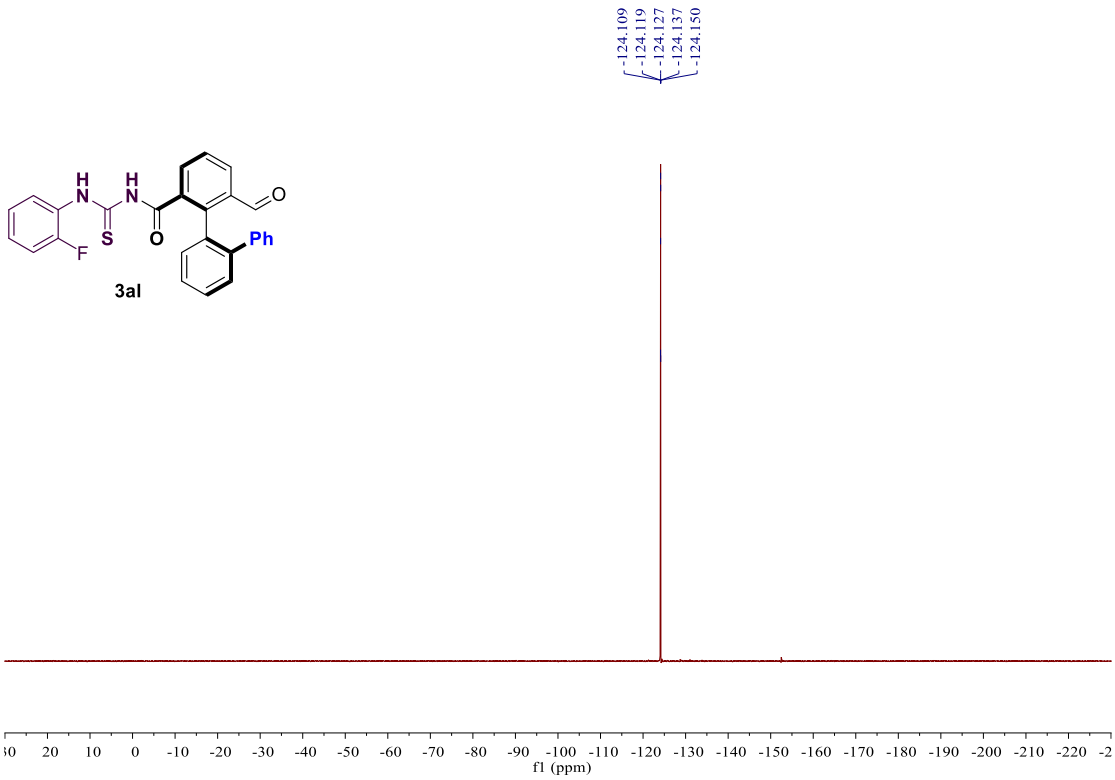
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ak.



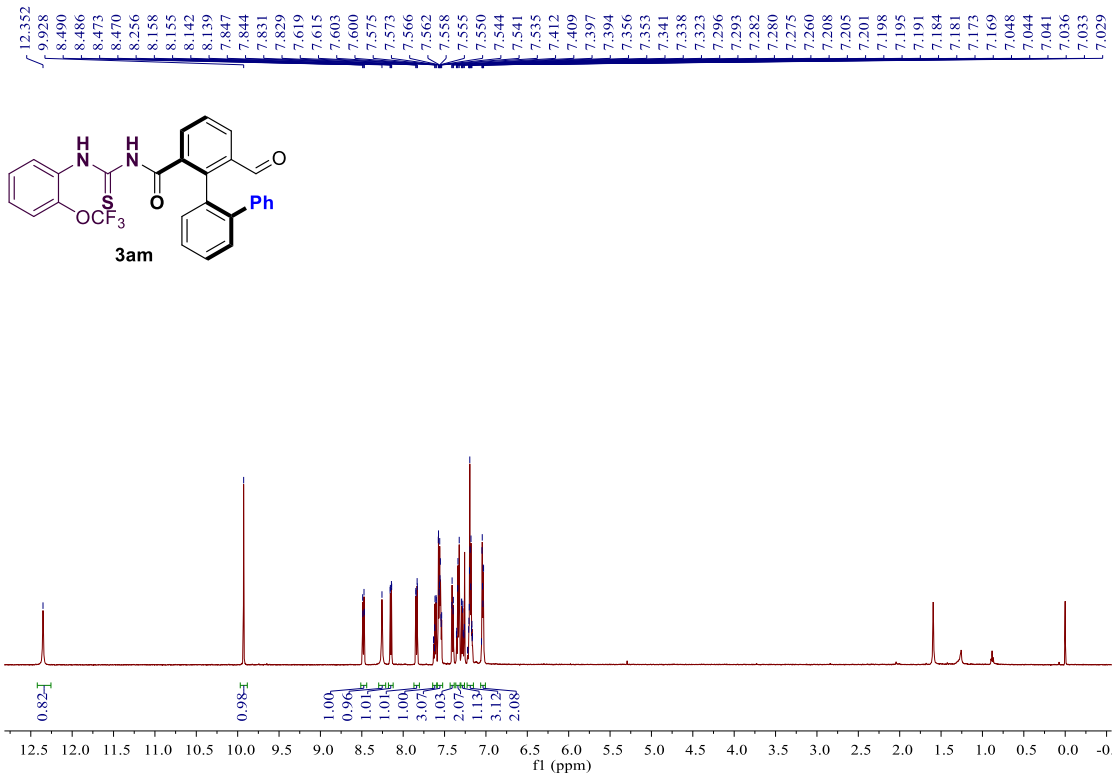
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3al.



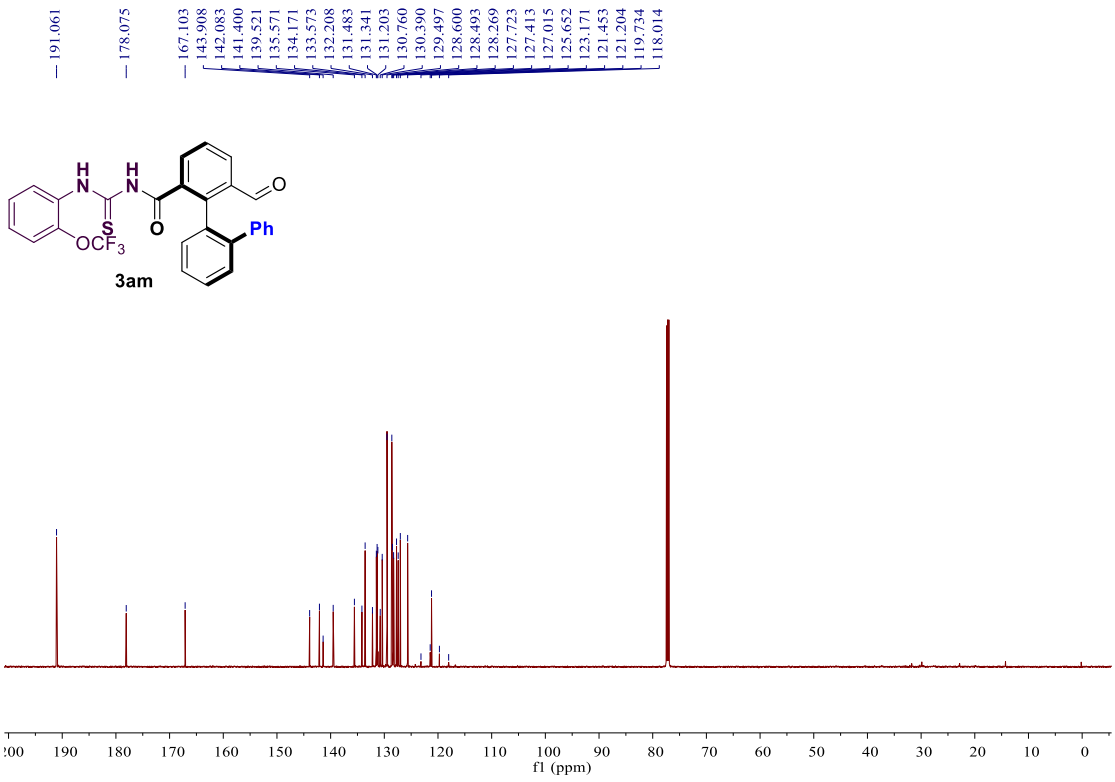
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3al.



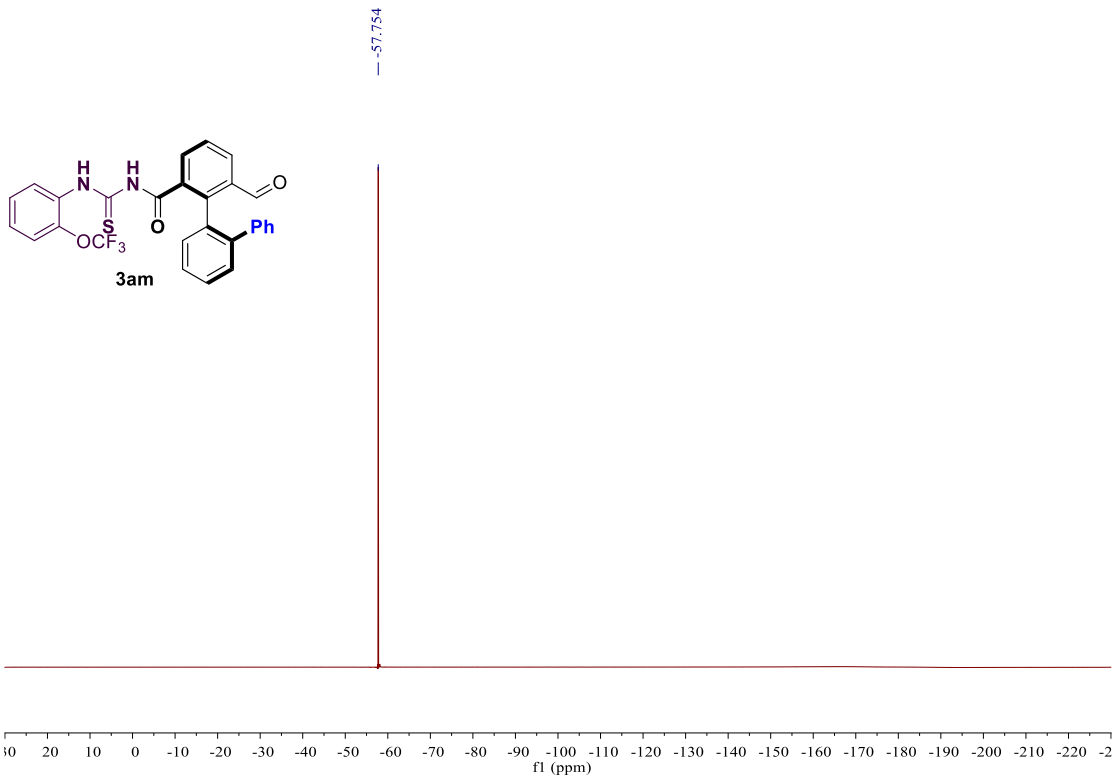
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3al.



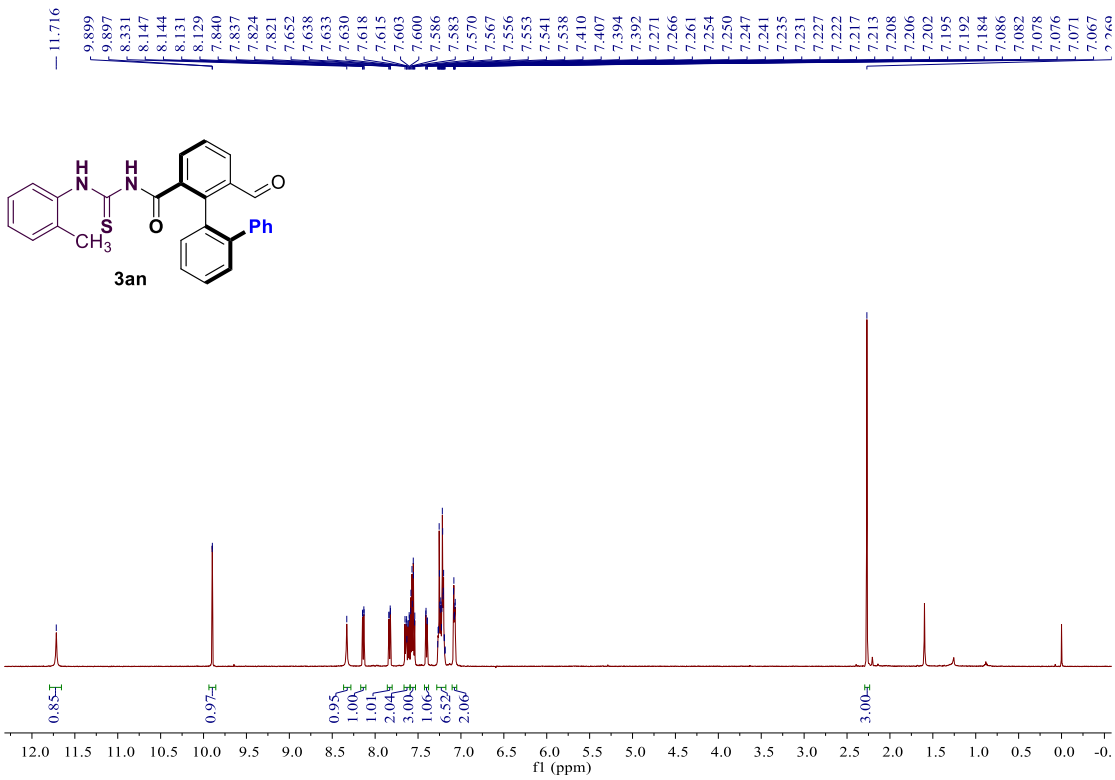
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3am.



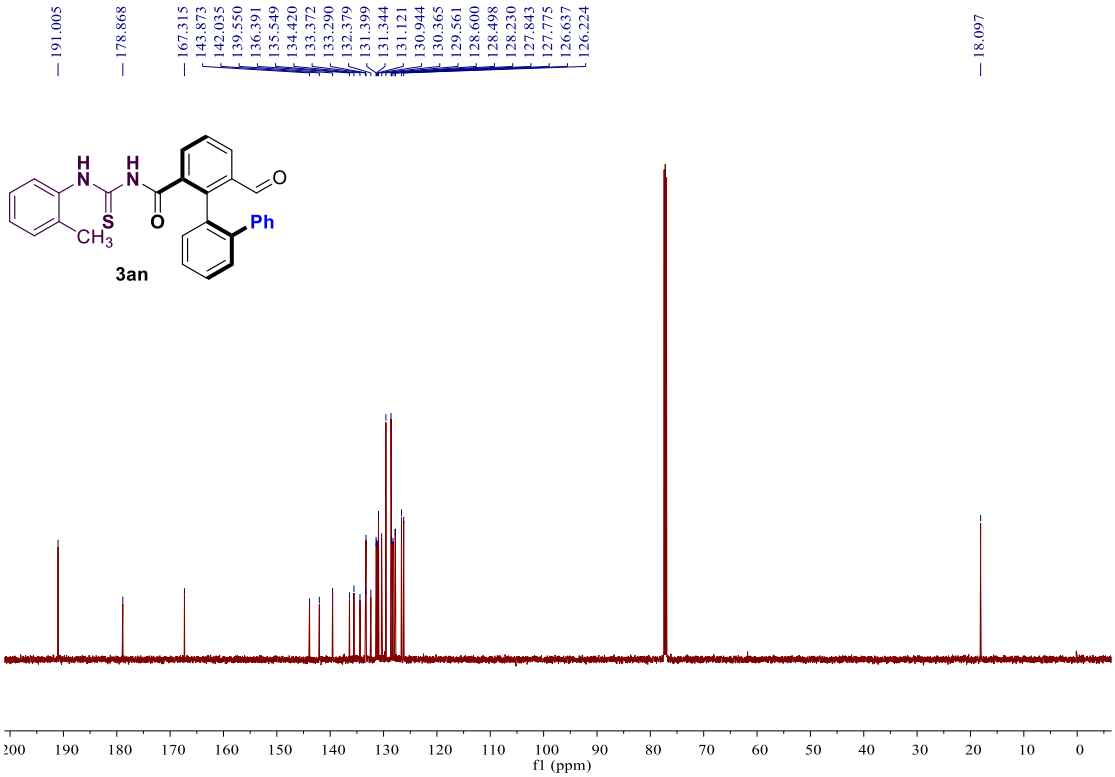
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3am.



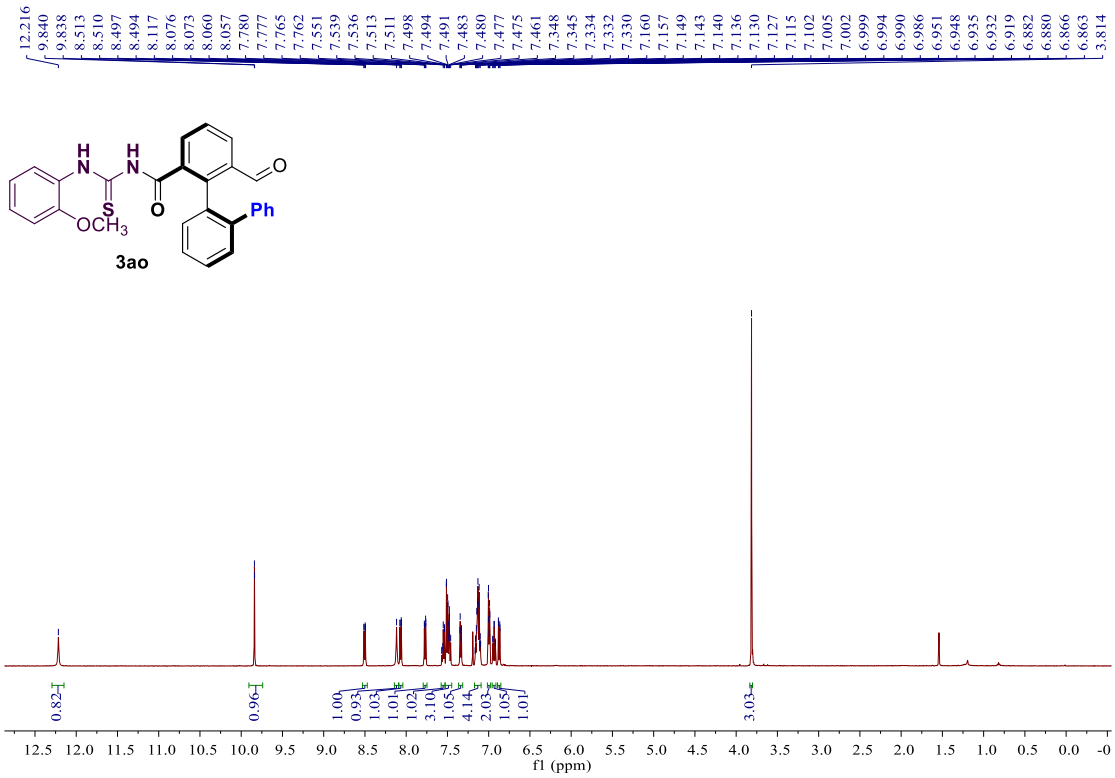
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3am.



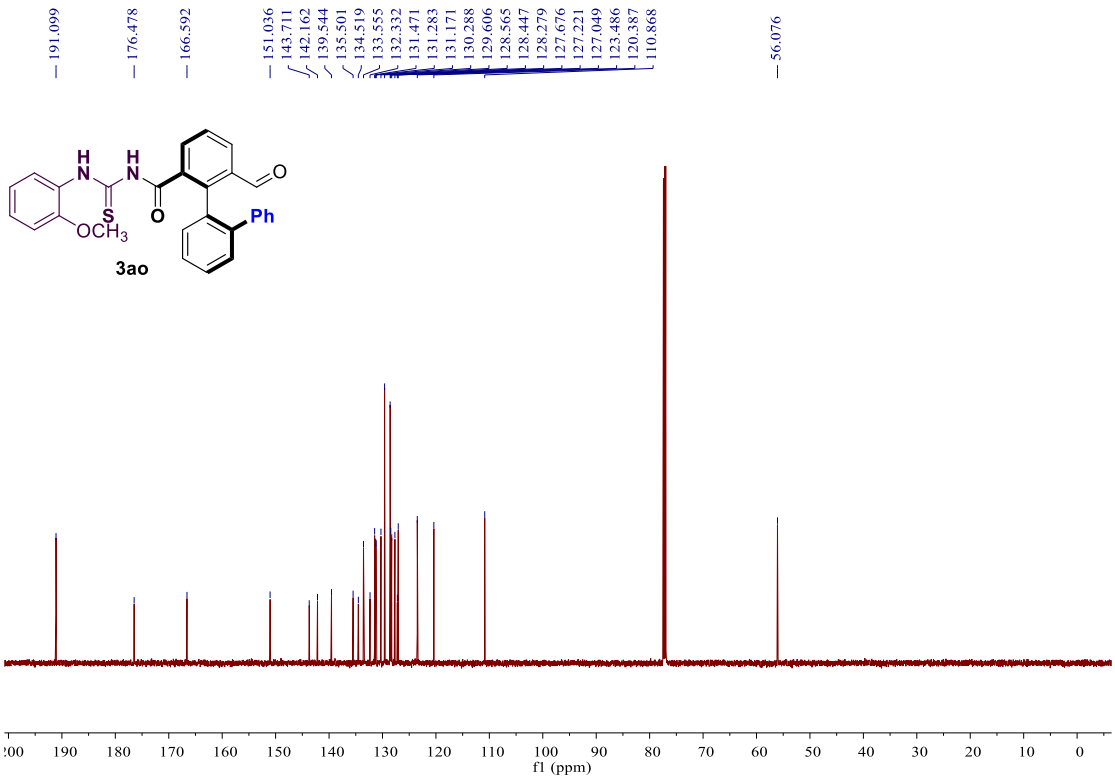
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3an.



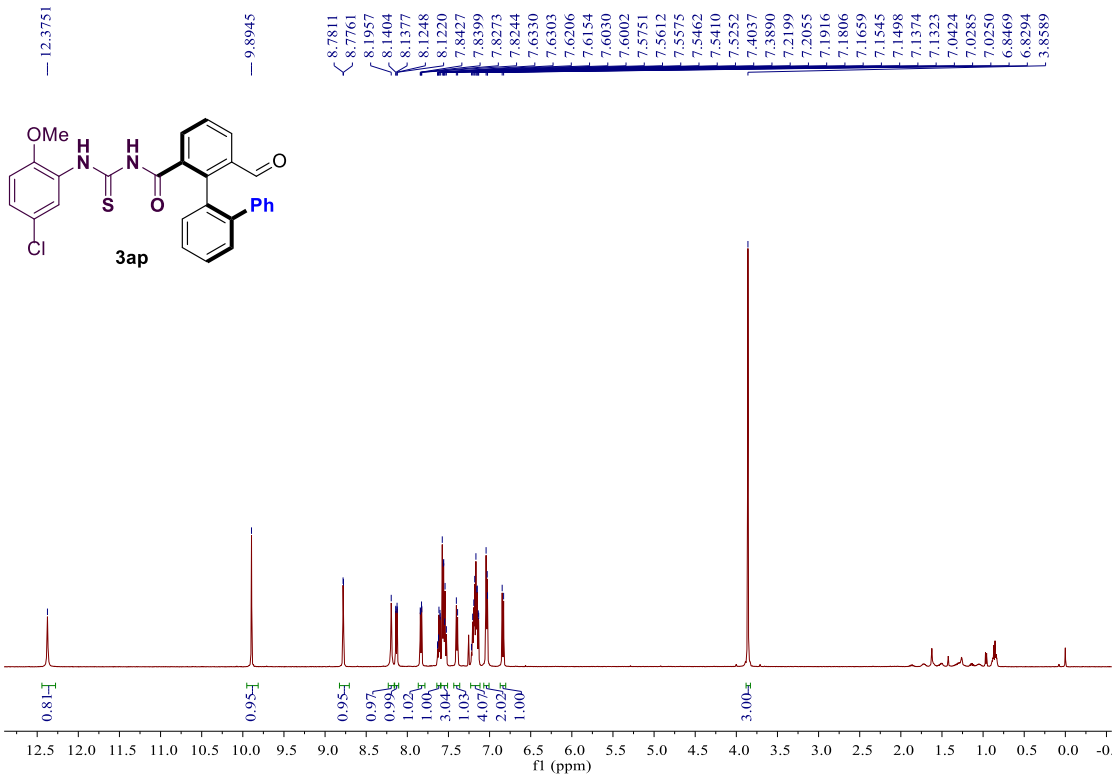
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3an.



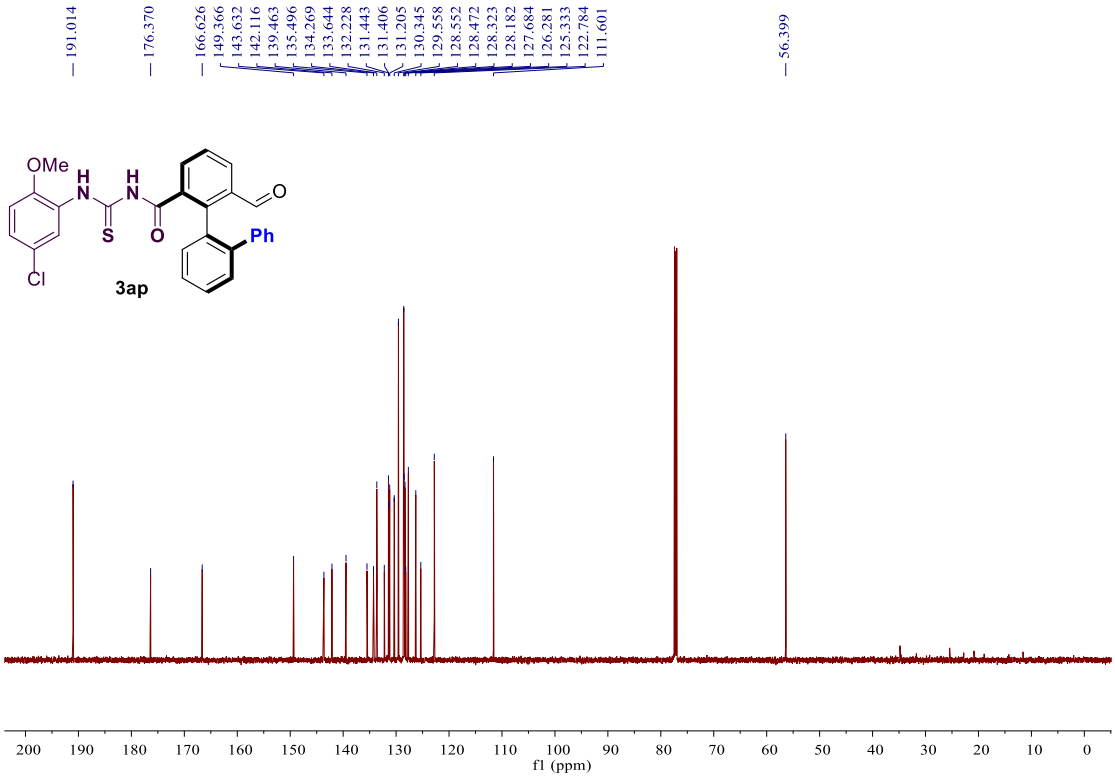
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ao.



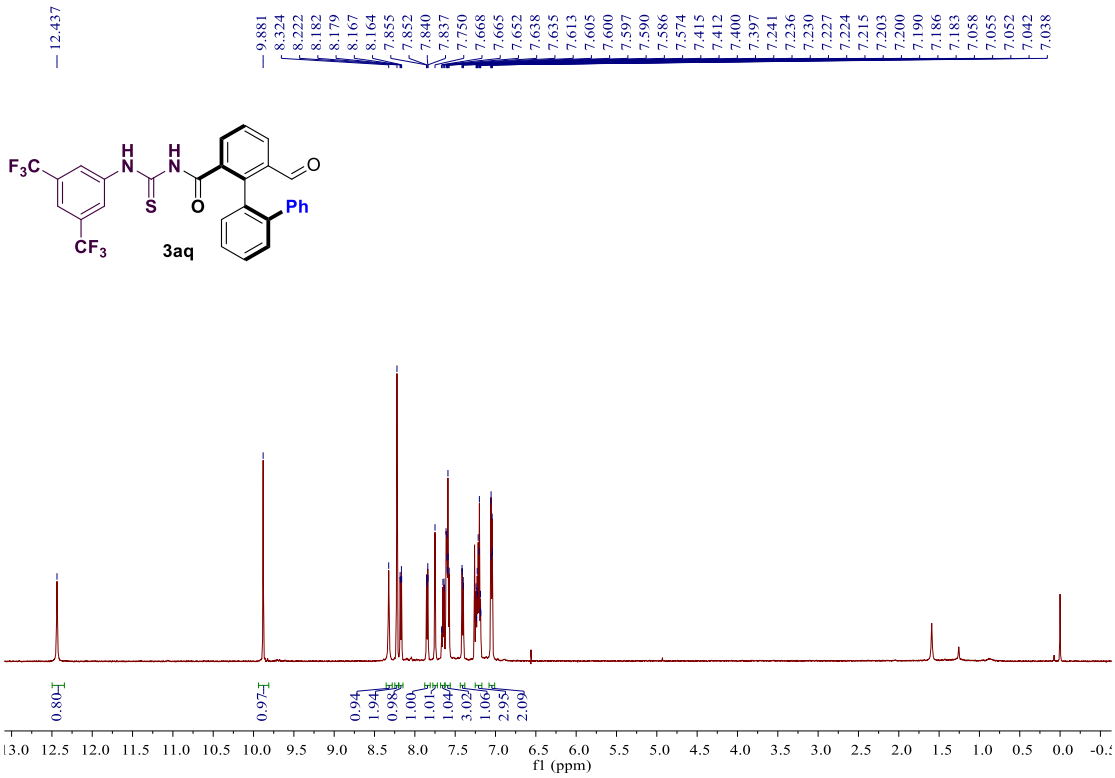
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ao.



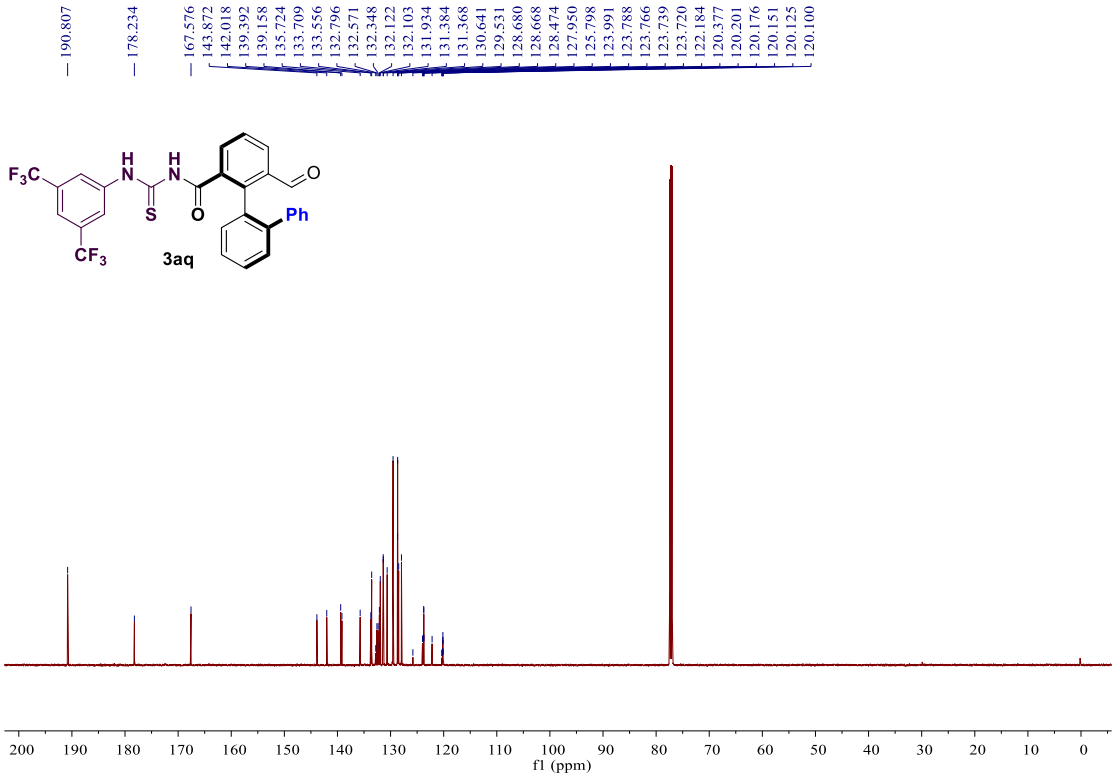
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3ap.



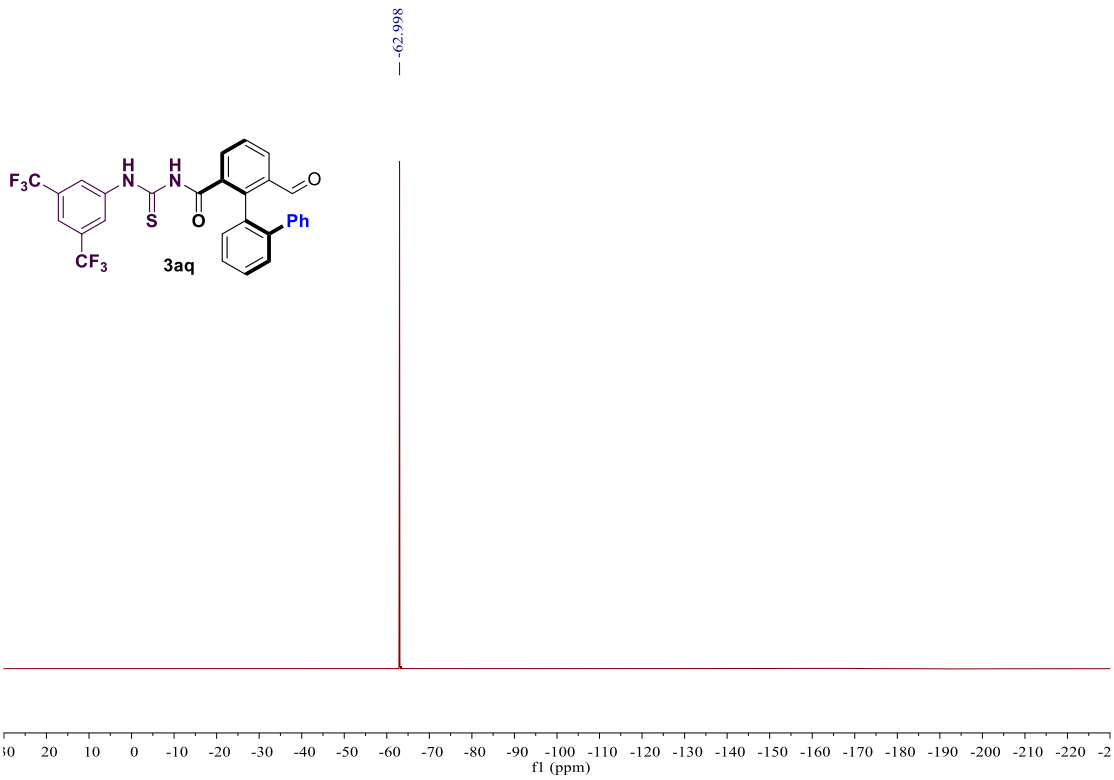
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3ap.



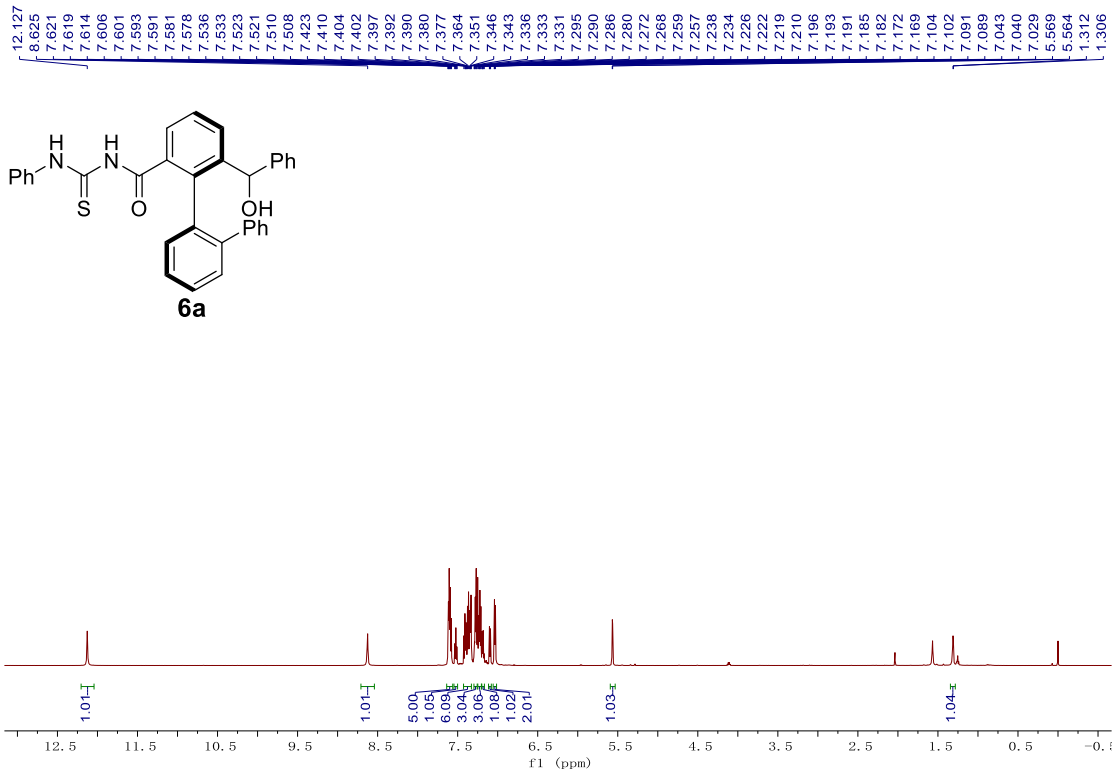
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 3aq.



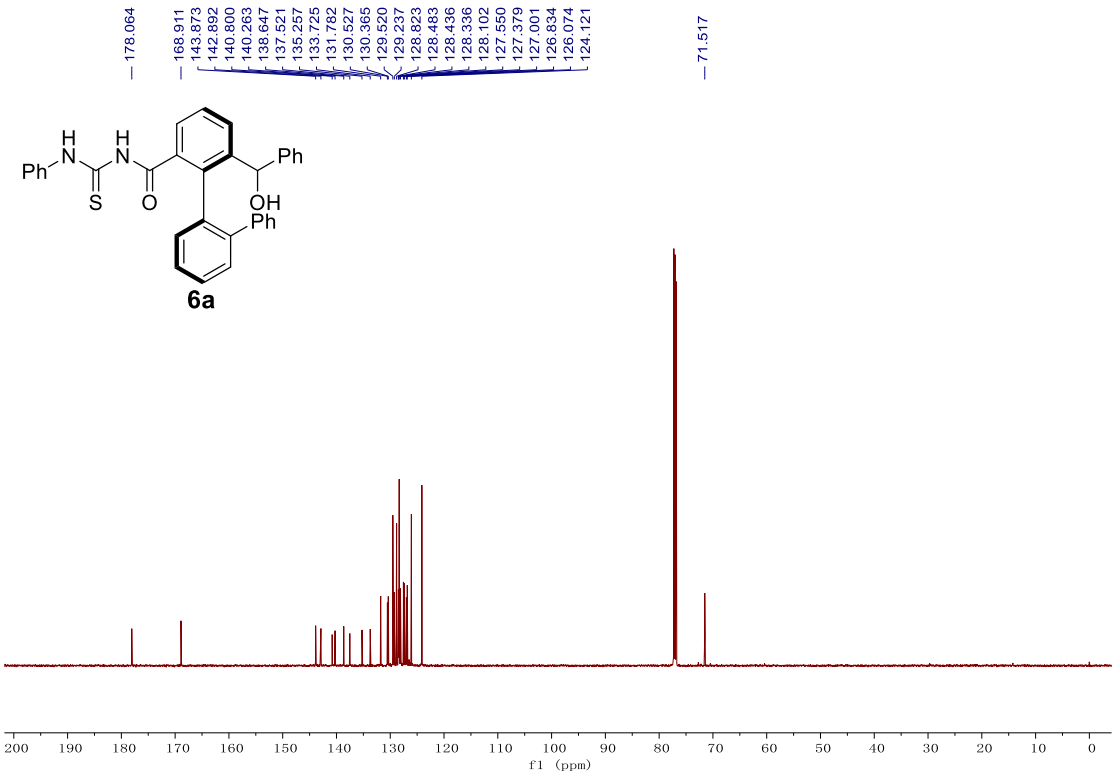
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 3aq.



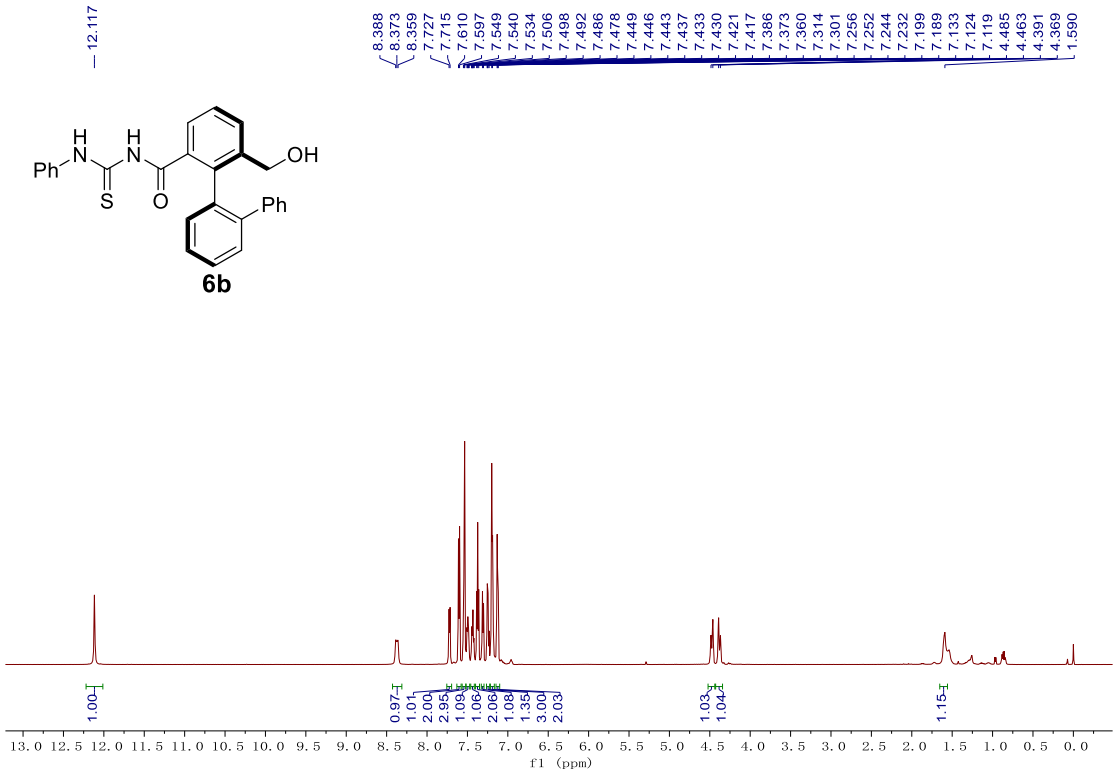
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 3aq.



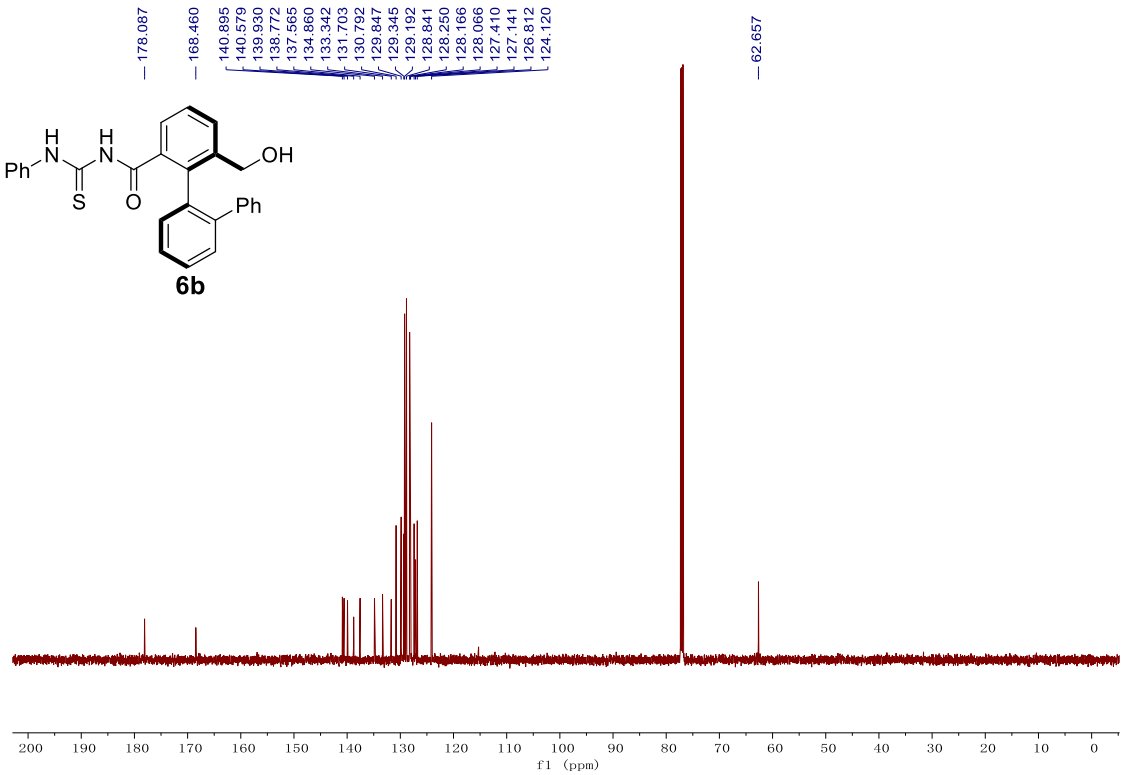
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6a.



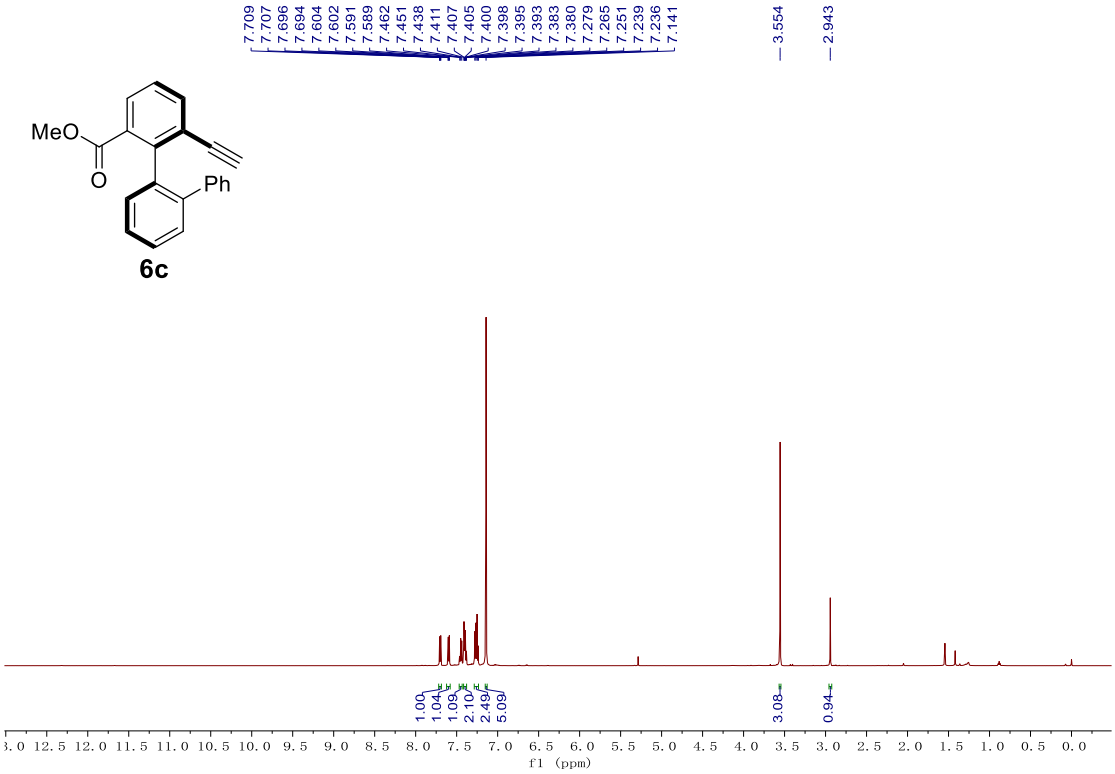
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 6a.



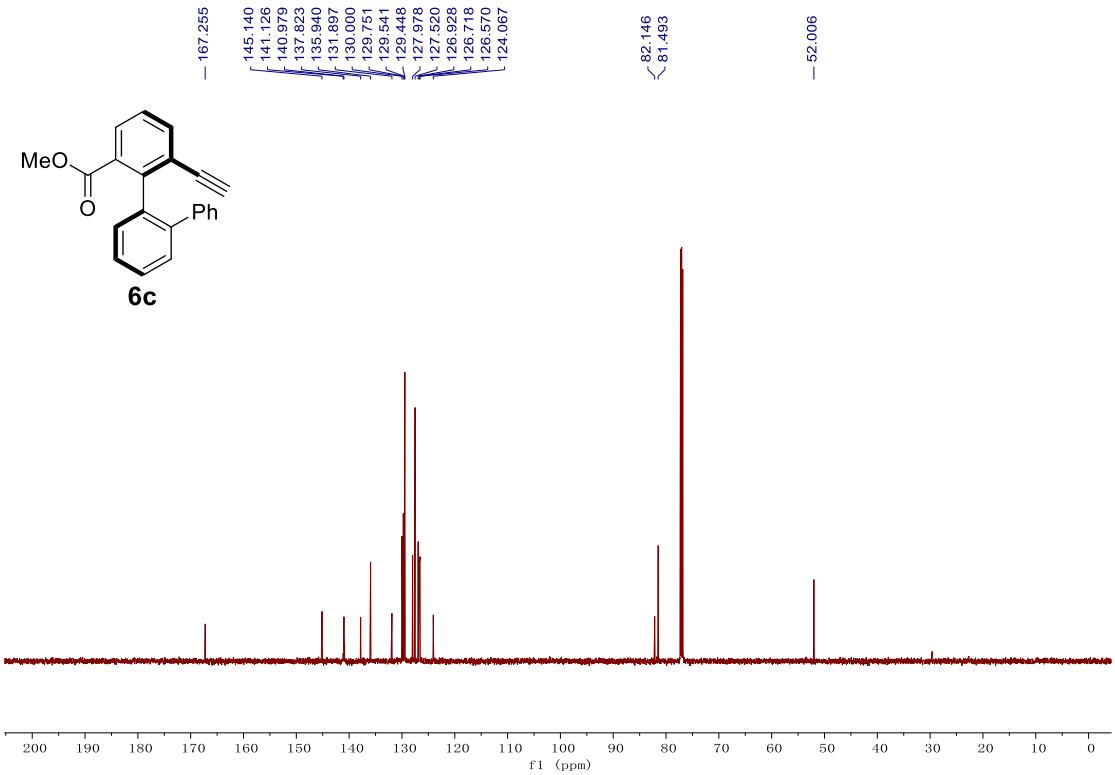
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6b.



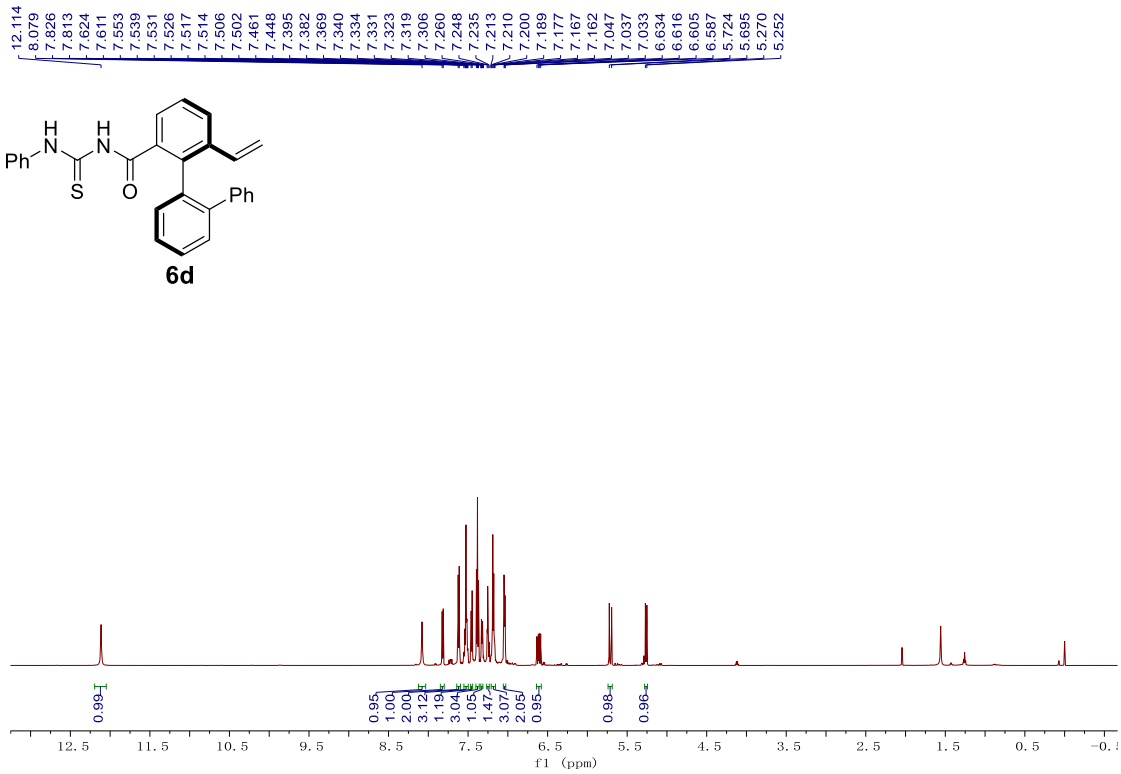
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 6b.



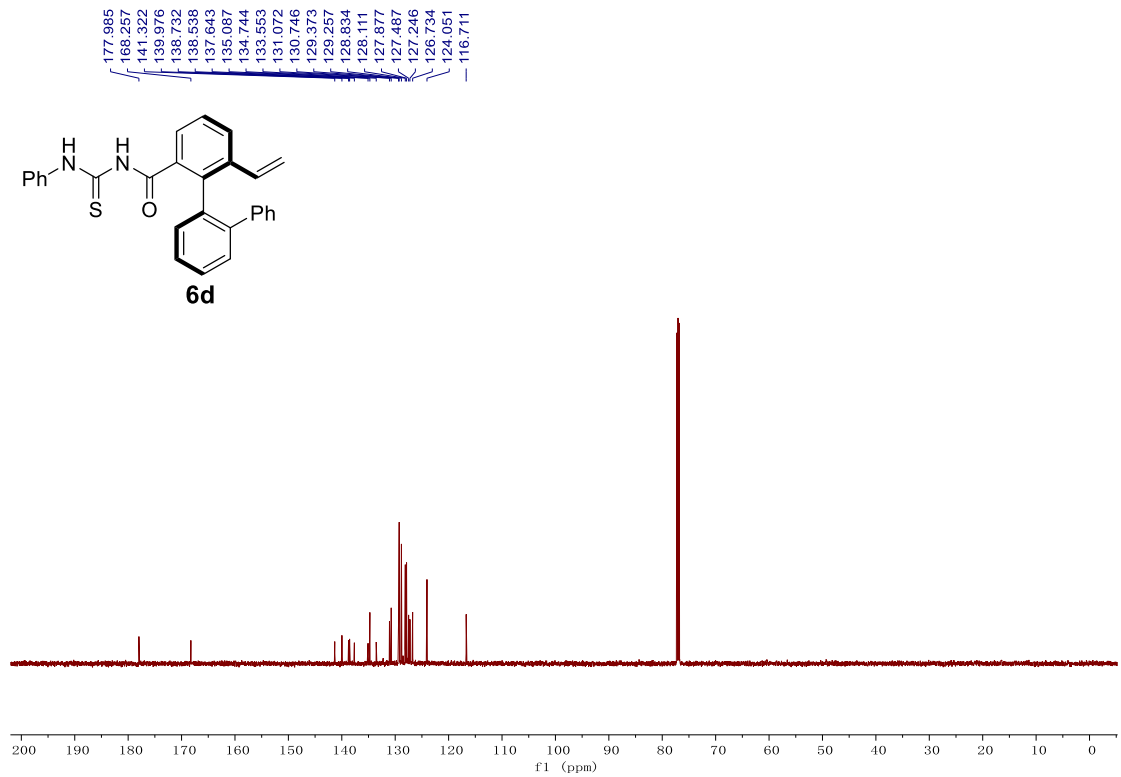
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6c.



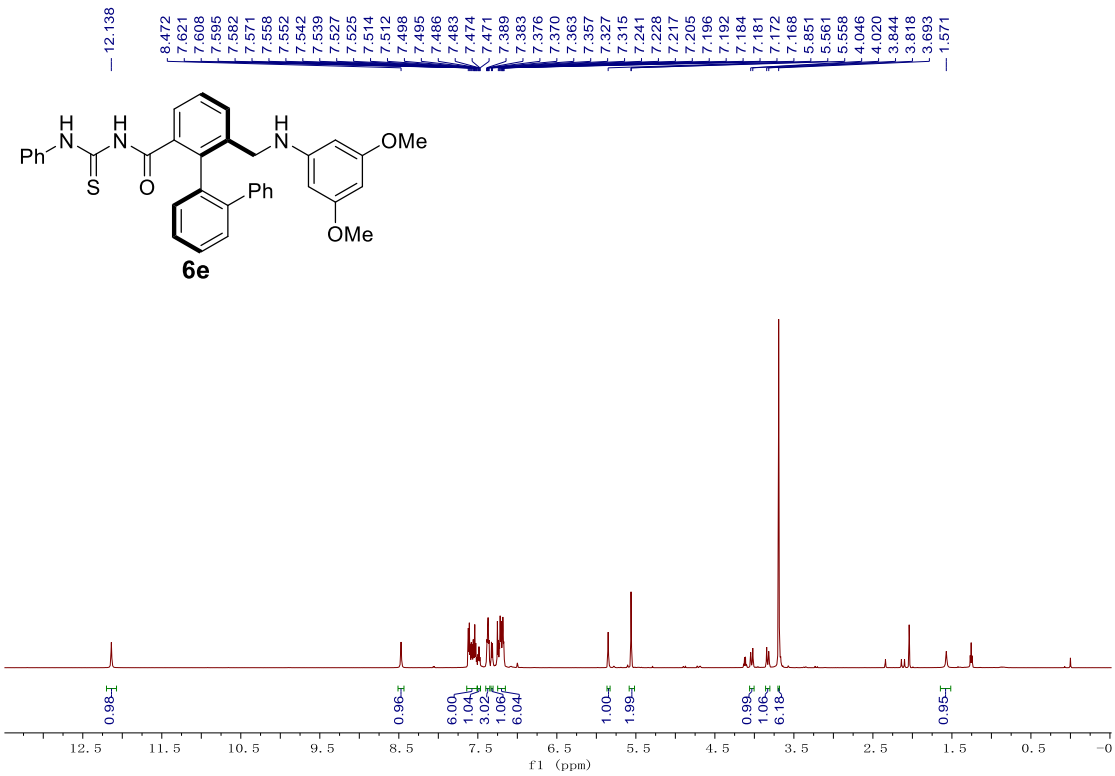
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 6c.



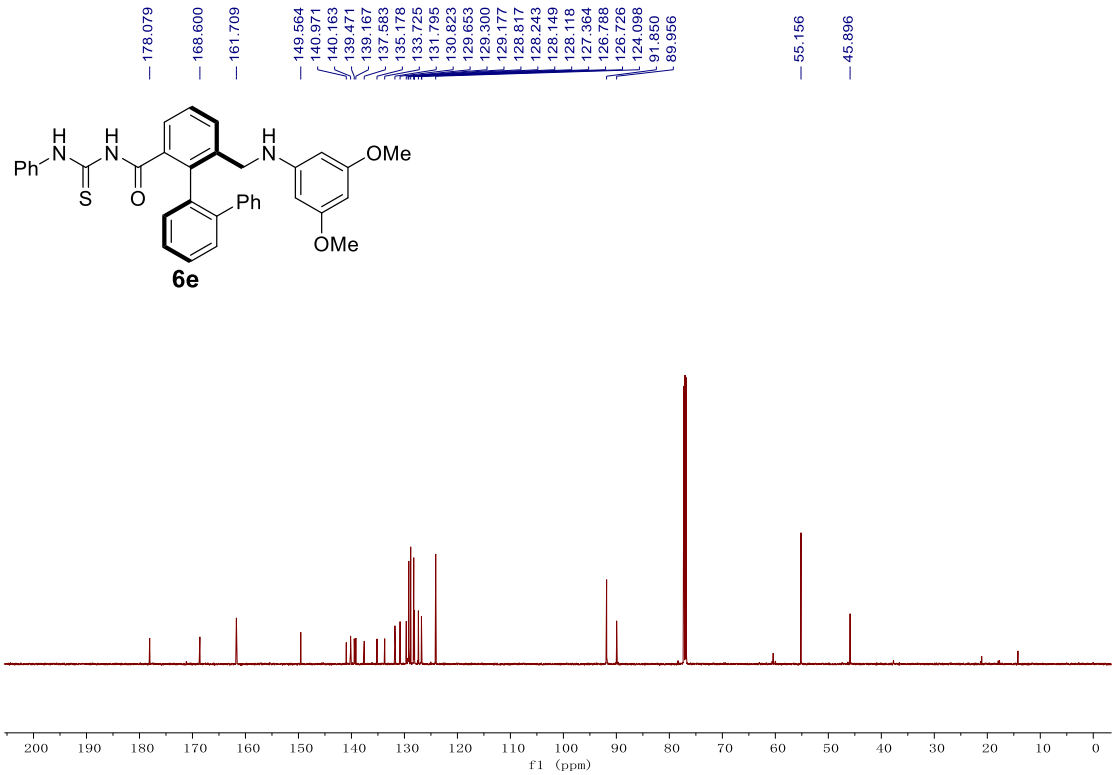
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6d.



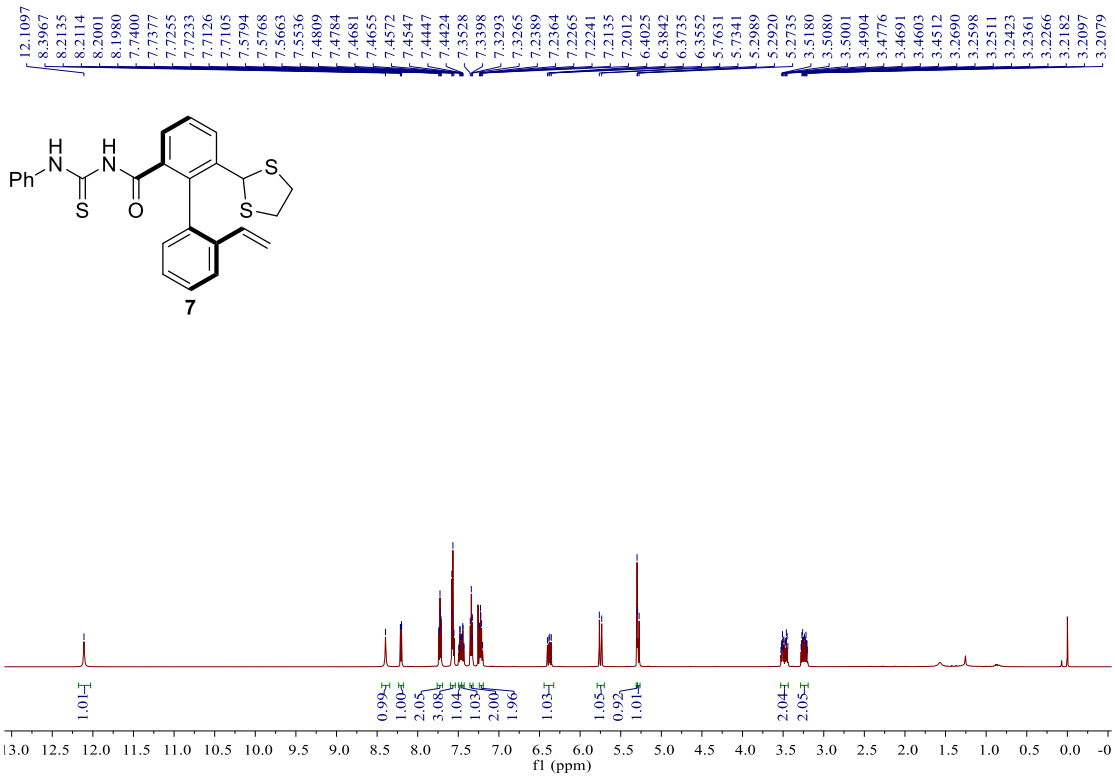
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 6d.



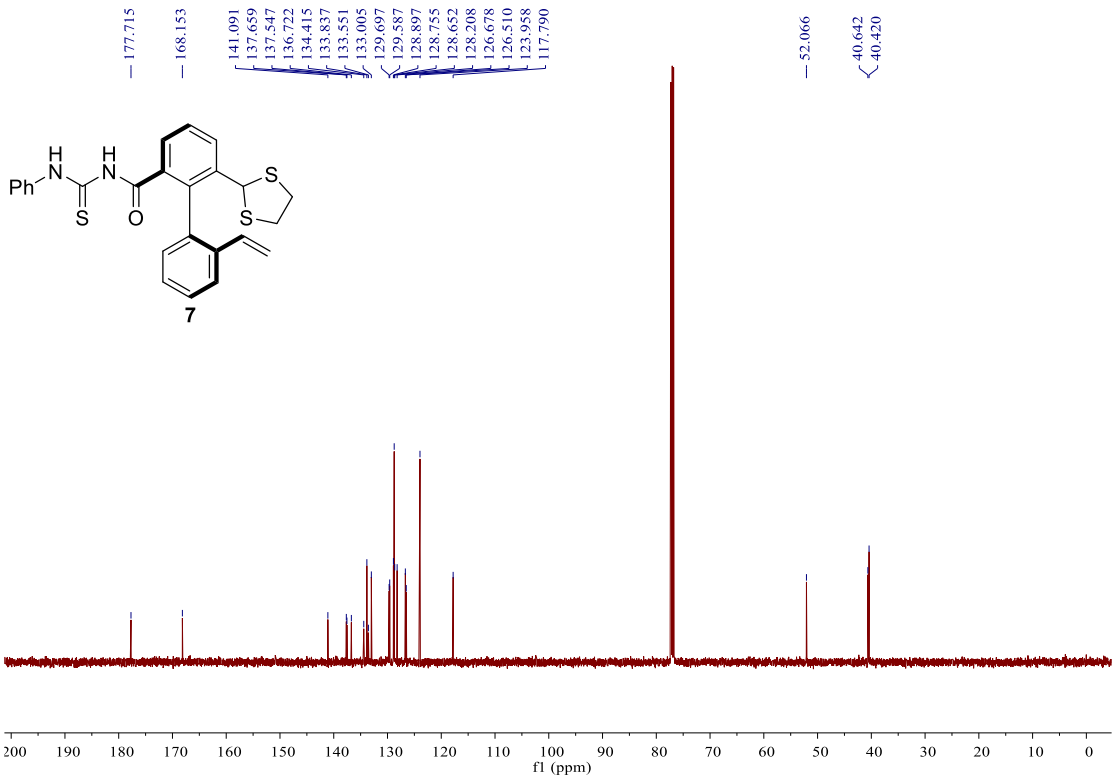
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 6e.



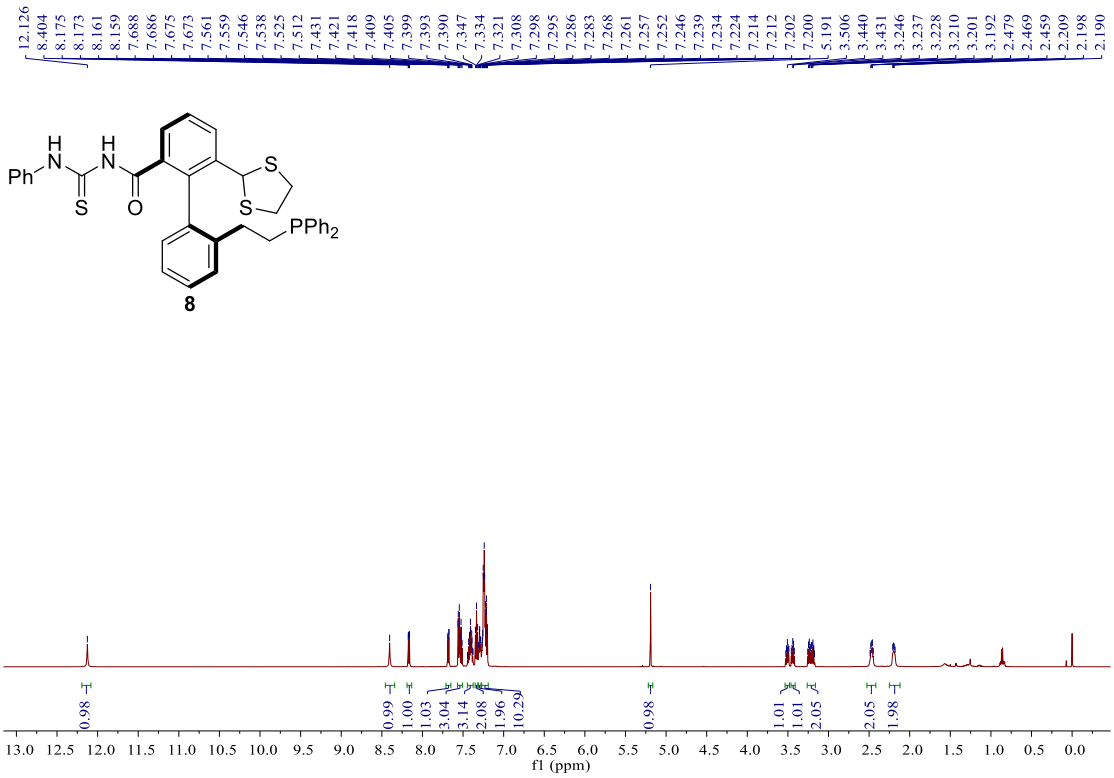
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 6e.



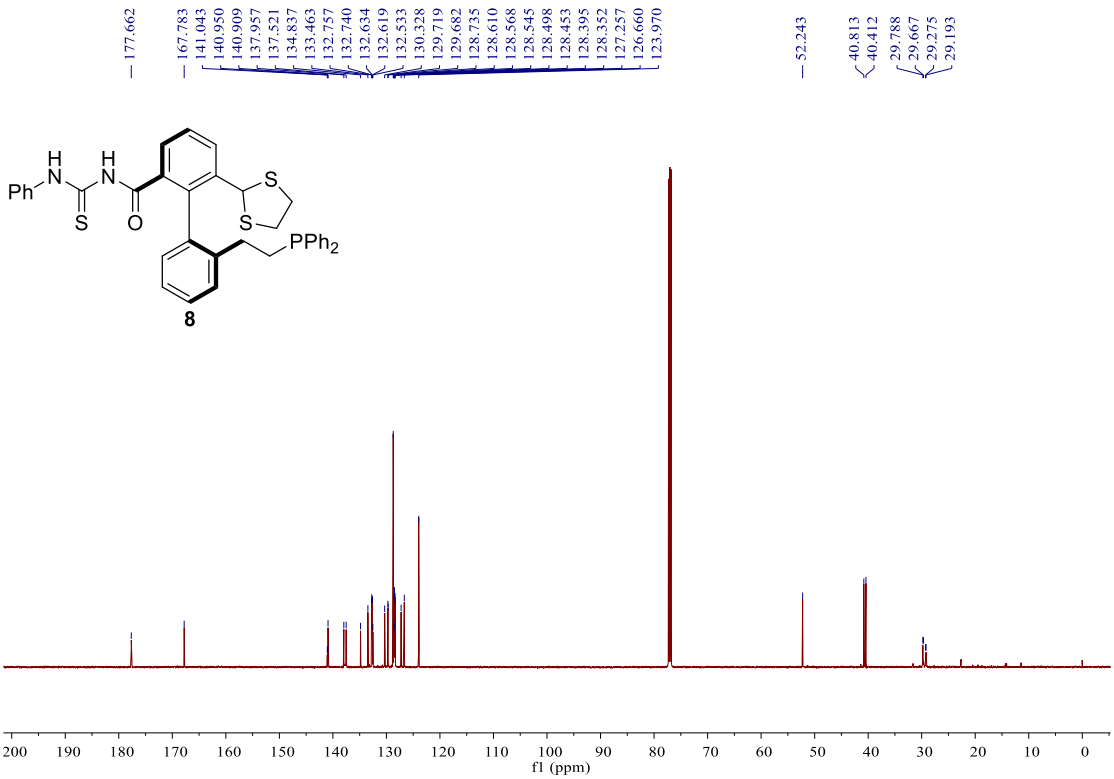
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 7.



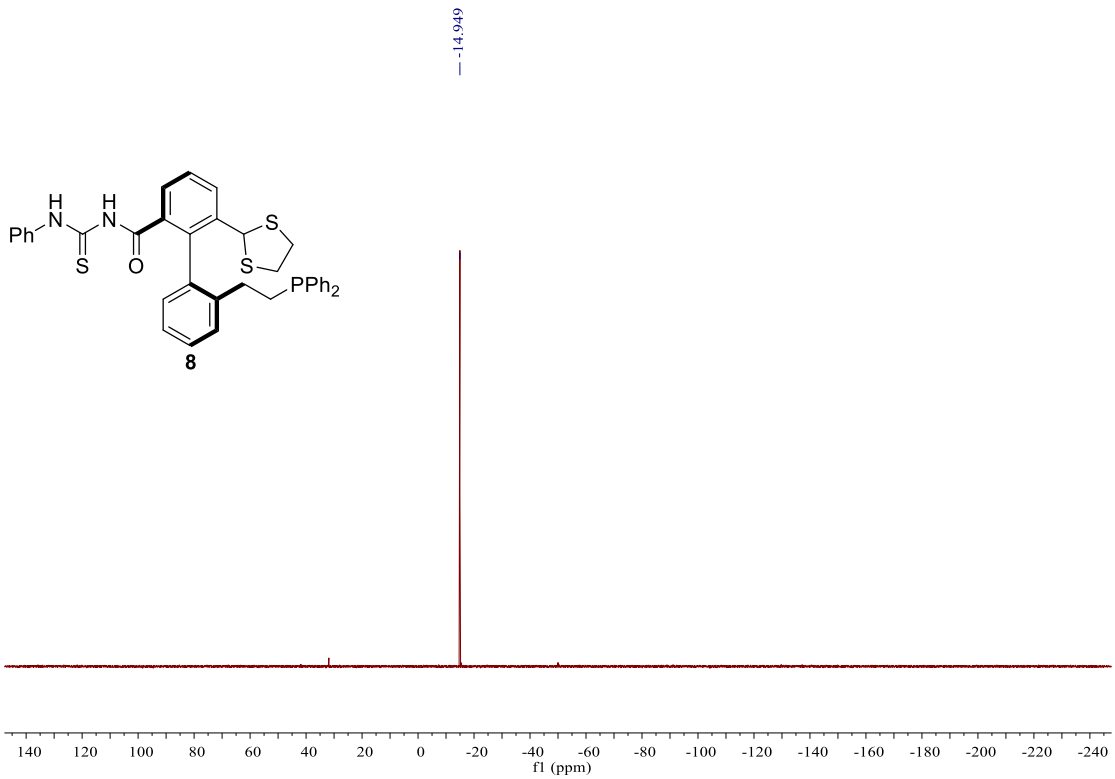
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of 7.



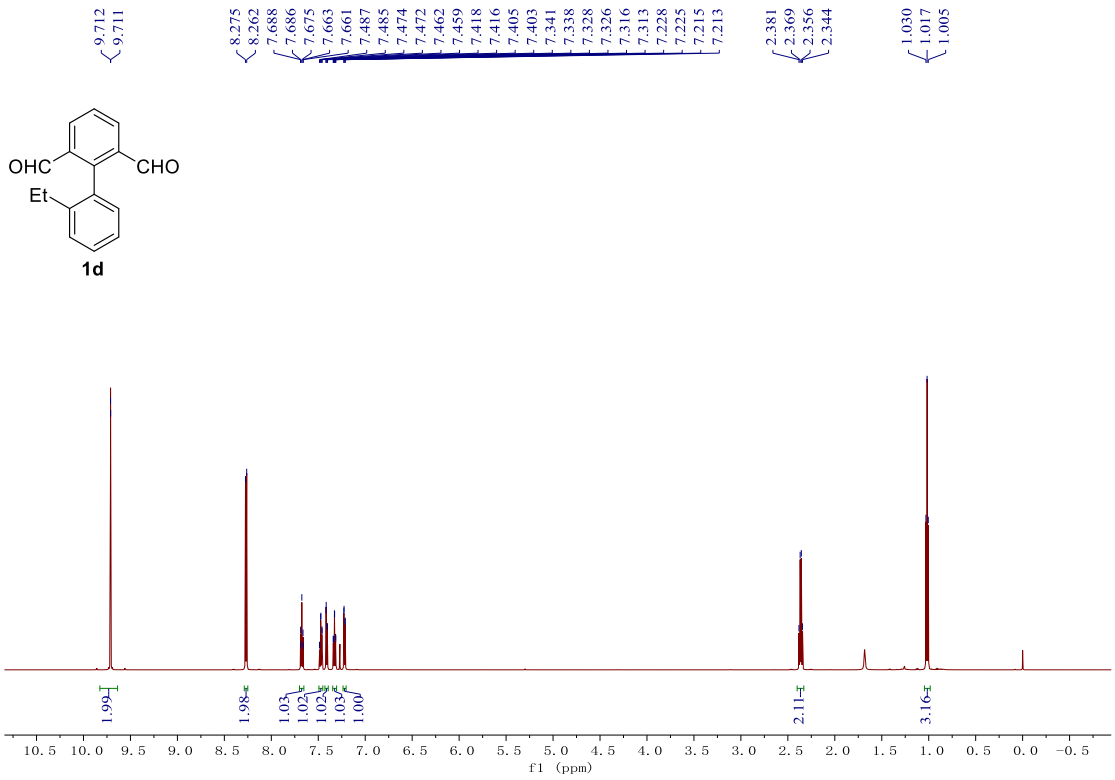
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 8.



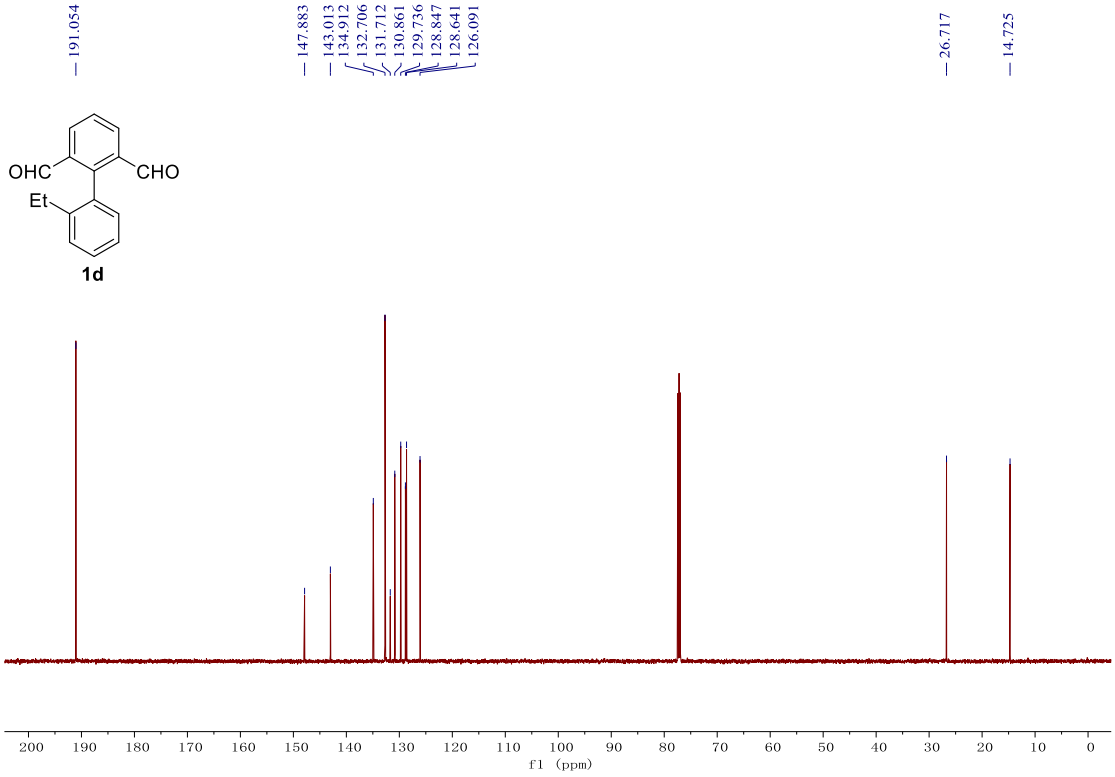
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 8.



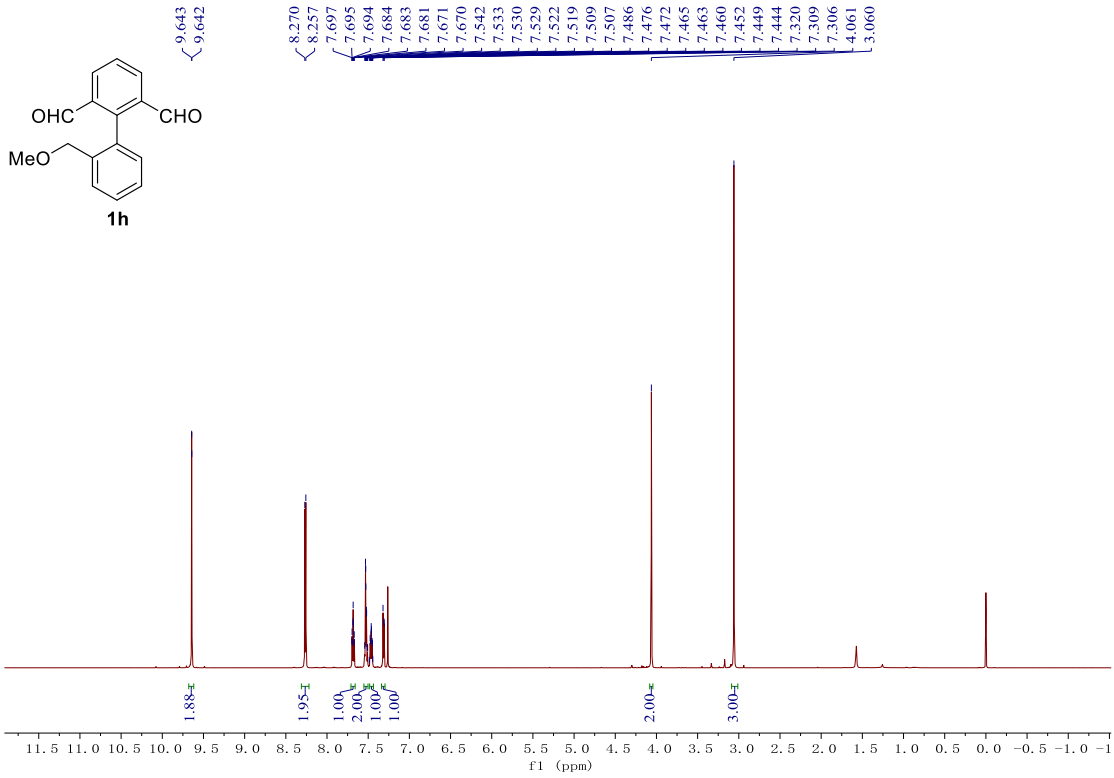
^{31}P NMR (243 MHz, $CDCl_3$) spectrum of 8.



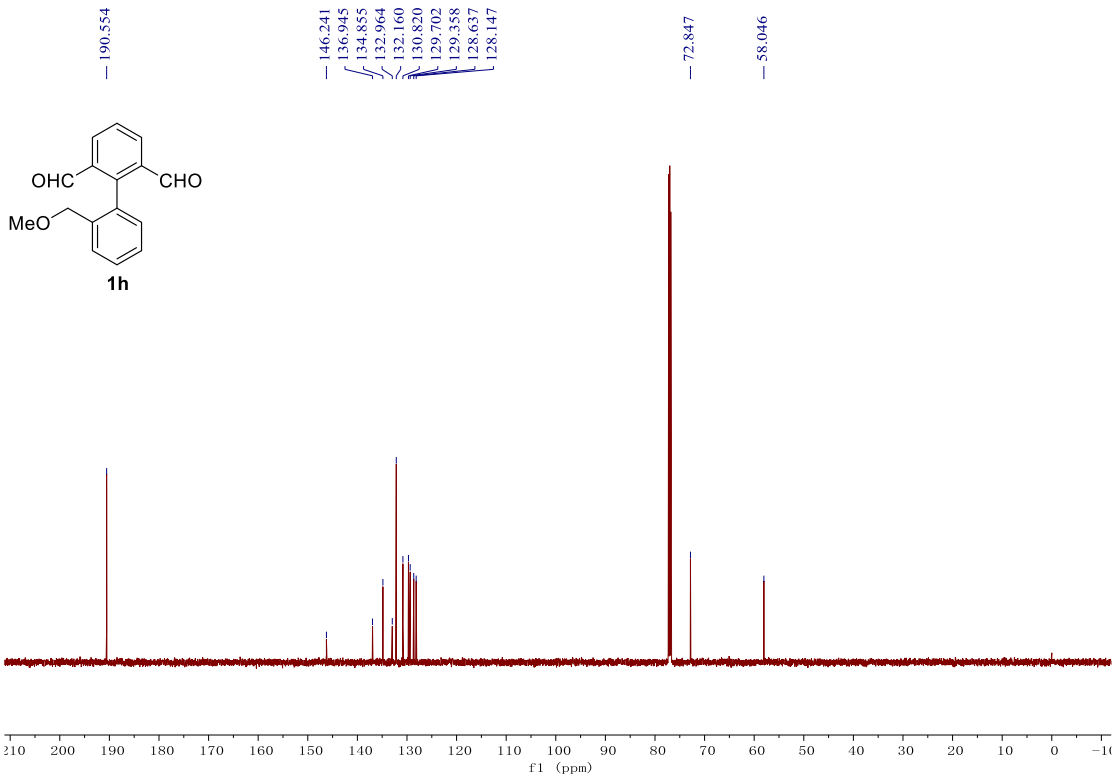
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1d.



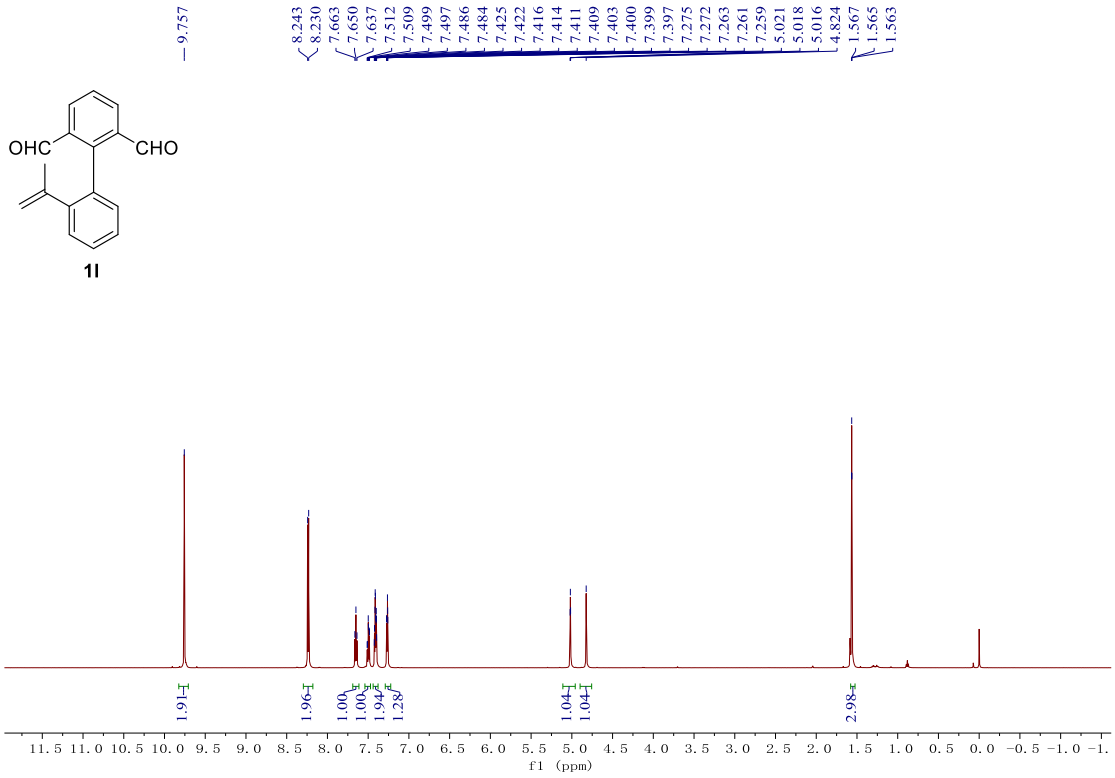
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1d.



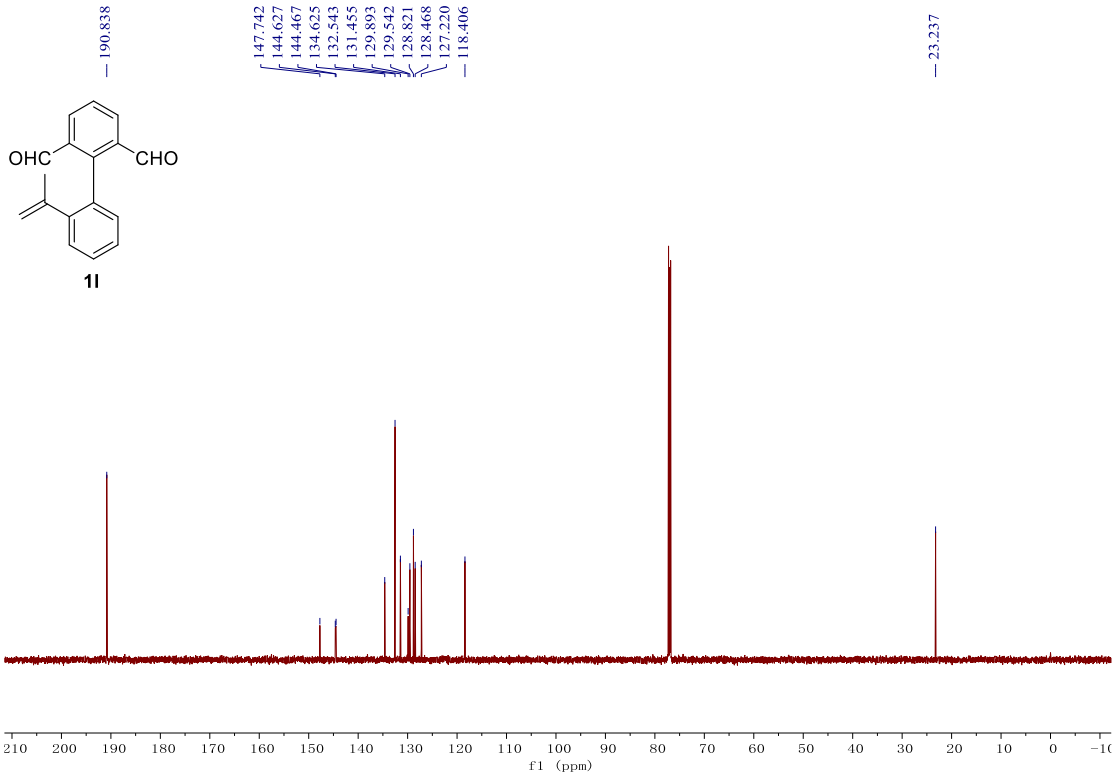
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1h.



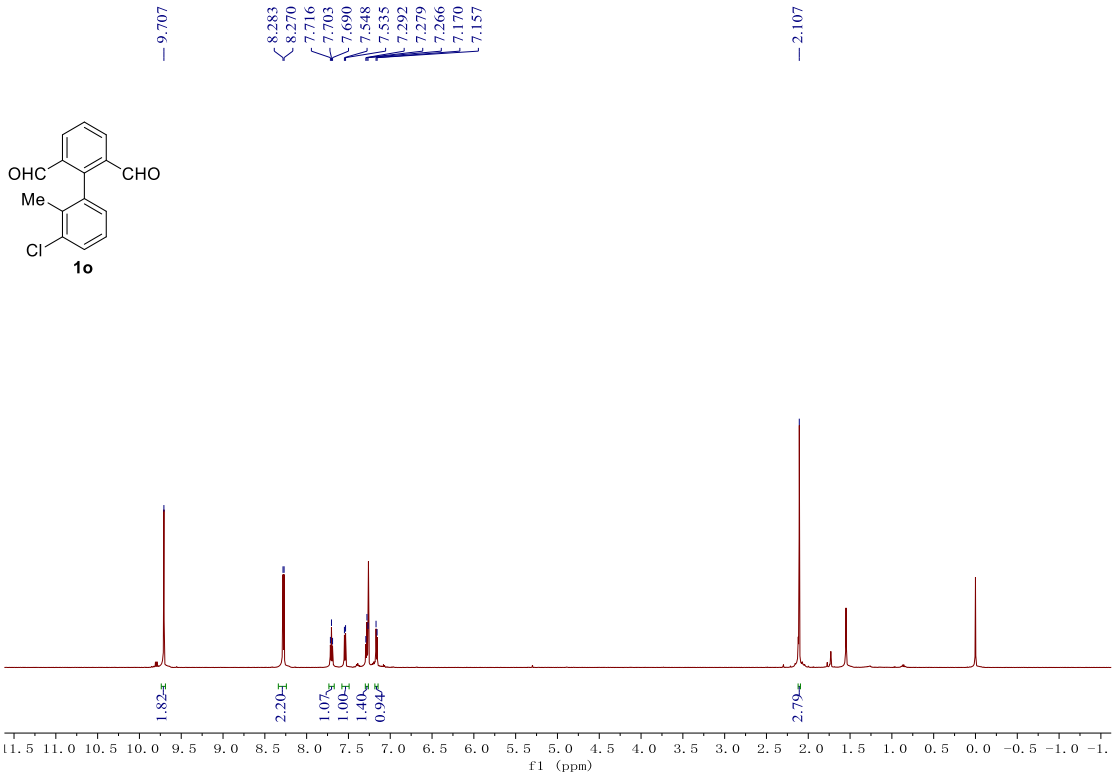
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1h.



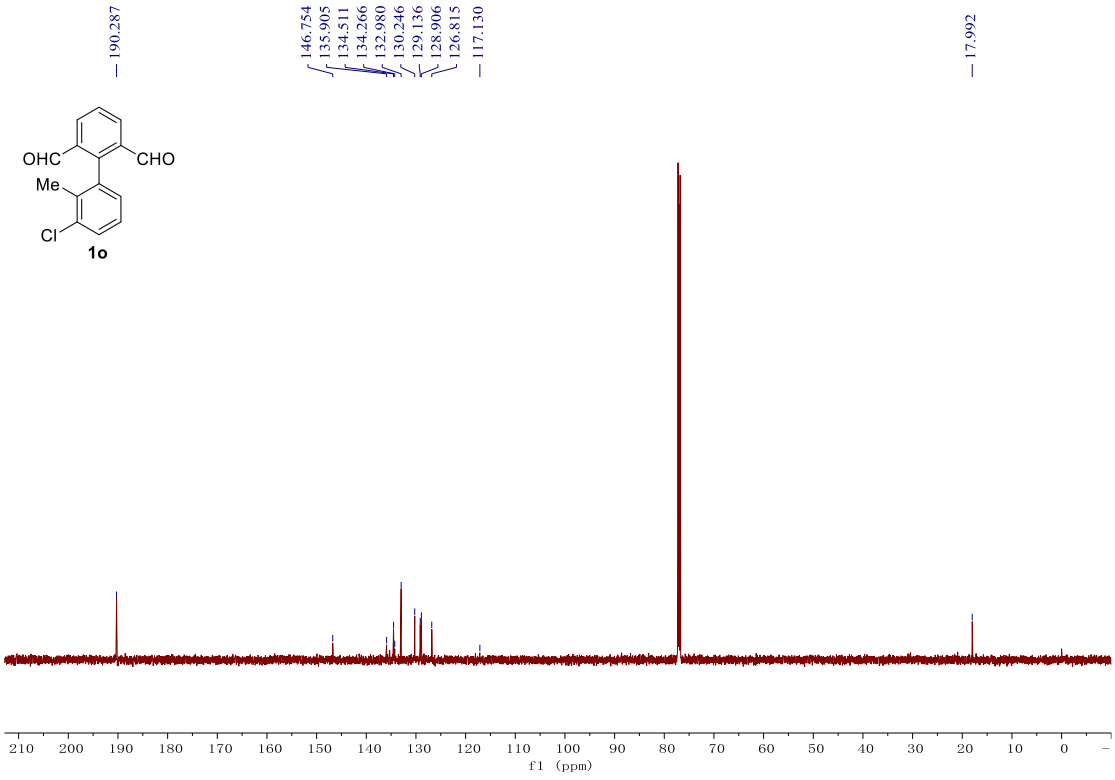
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1l.



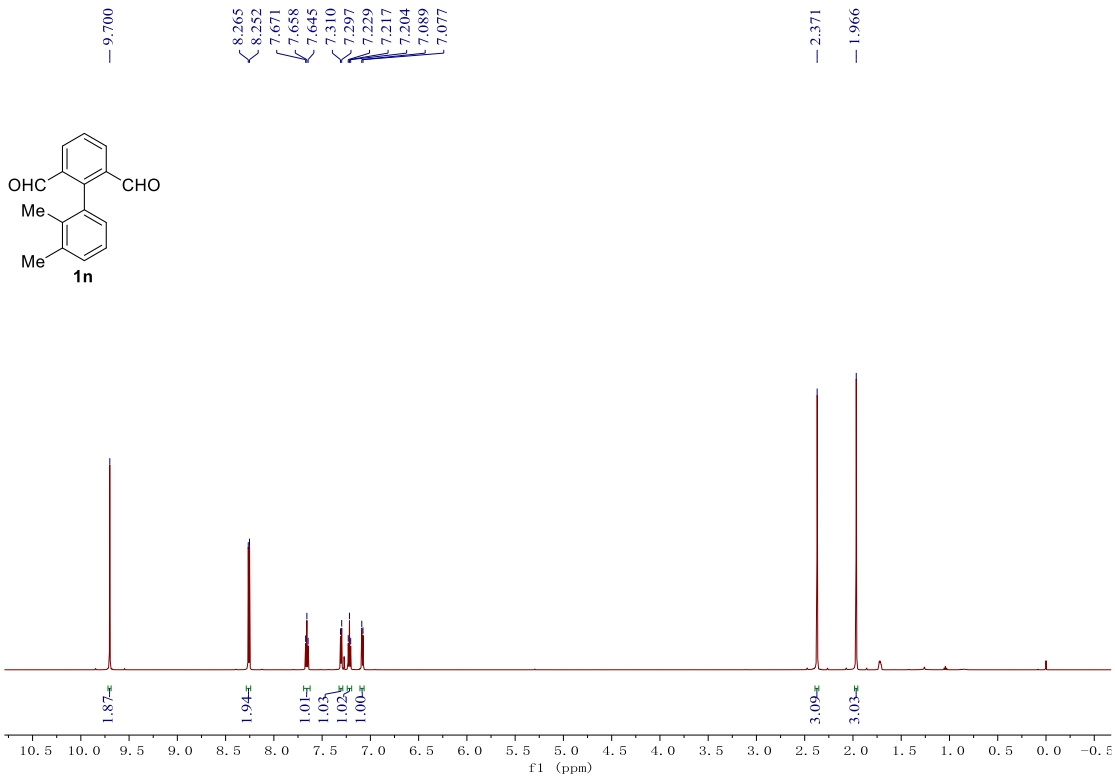
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1l.



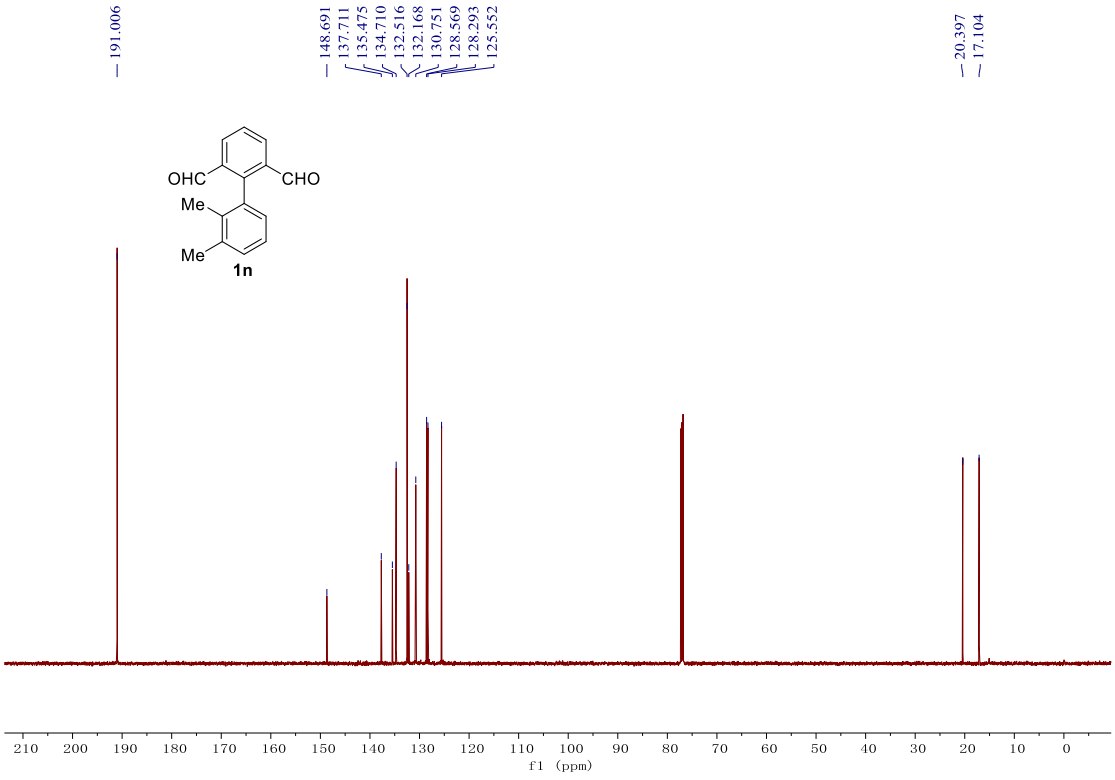
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1o.



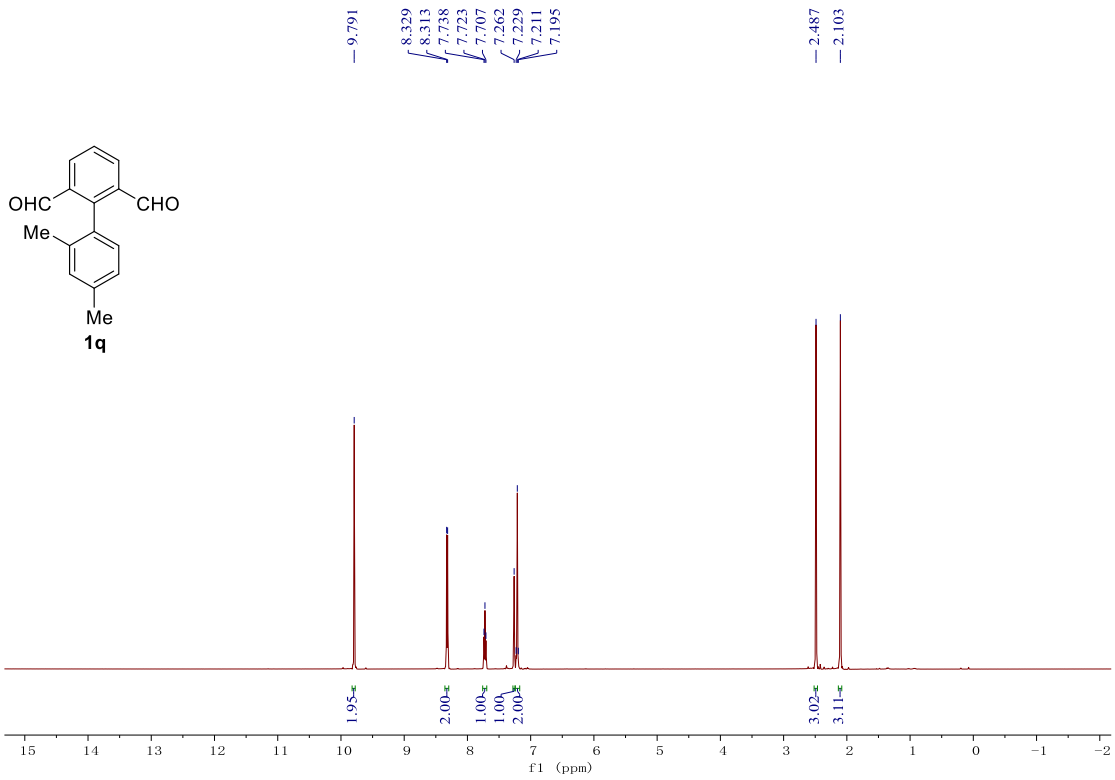
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1o.



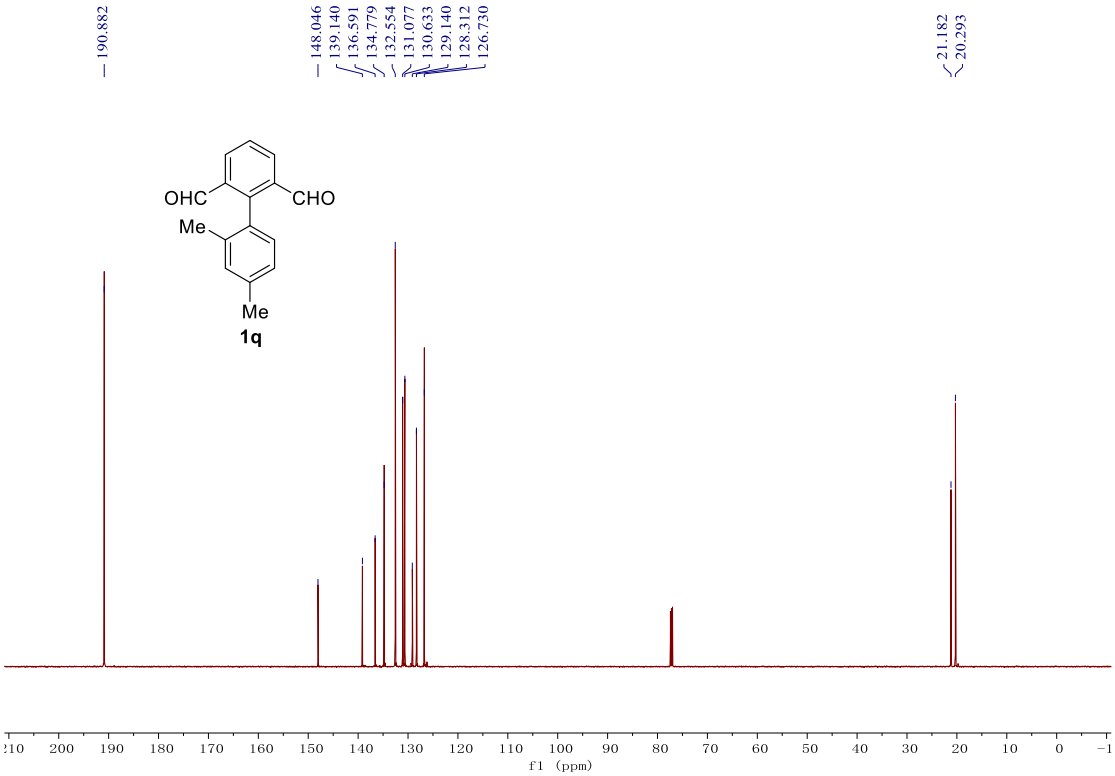
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1n.



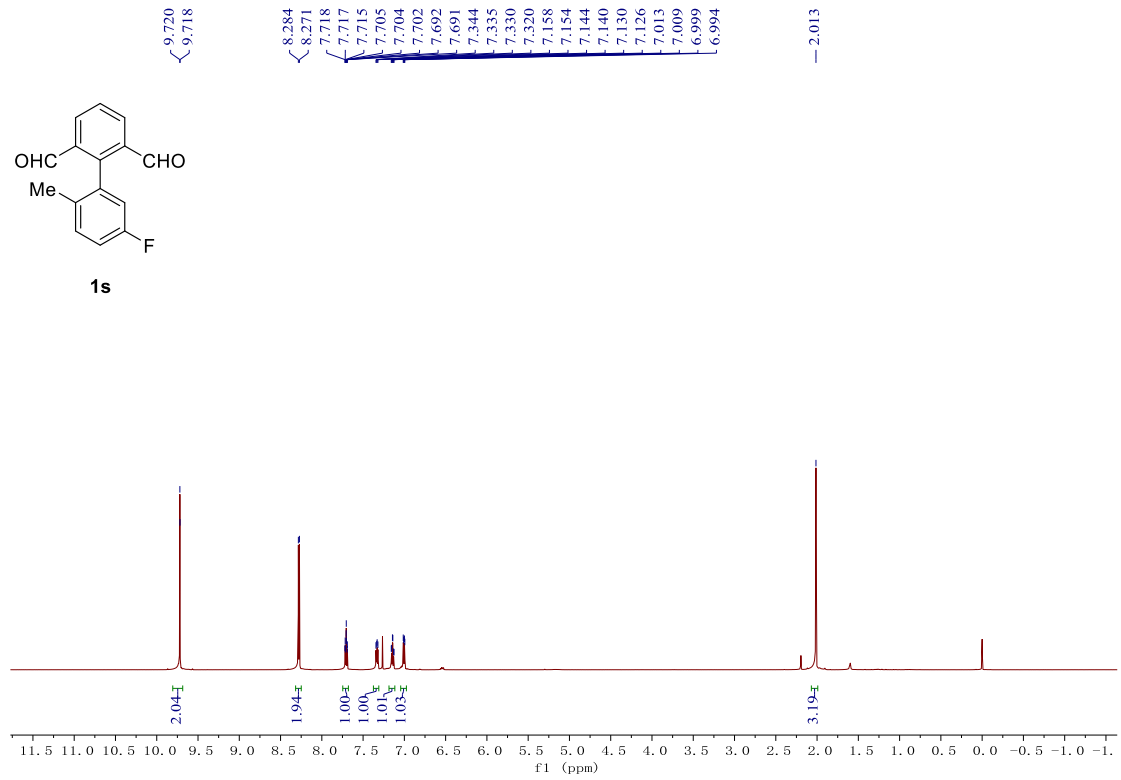
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1n.



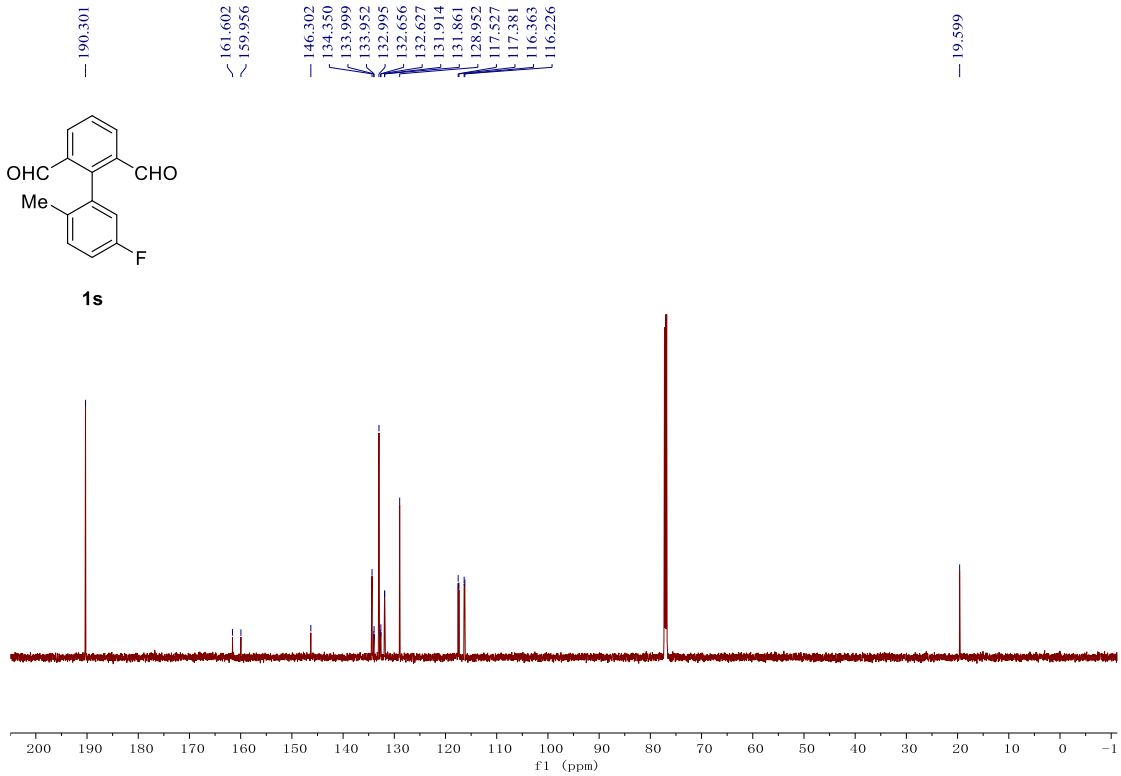
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1q.



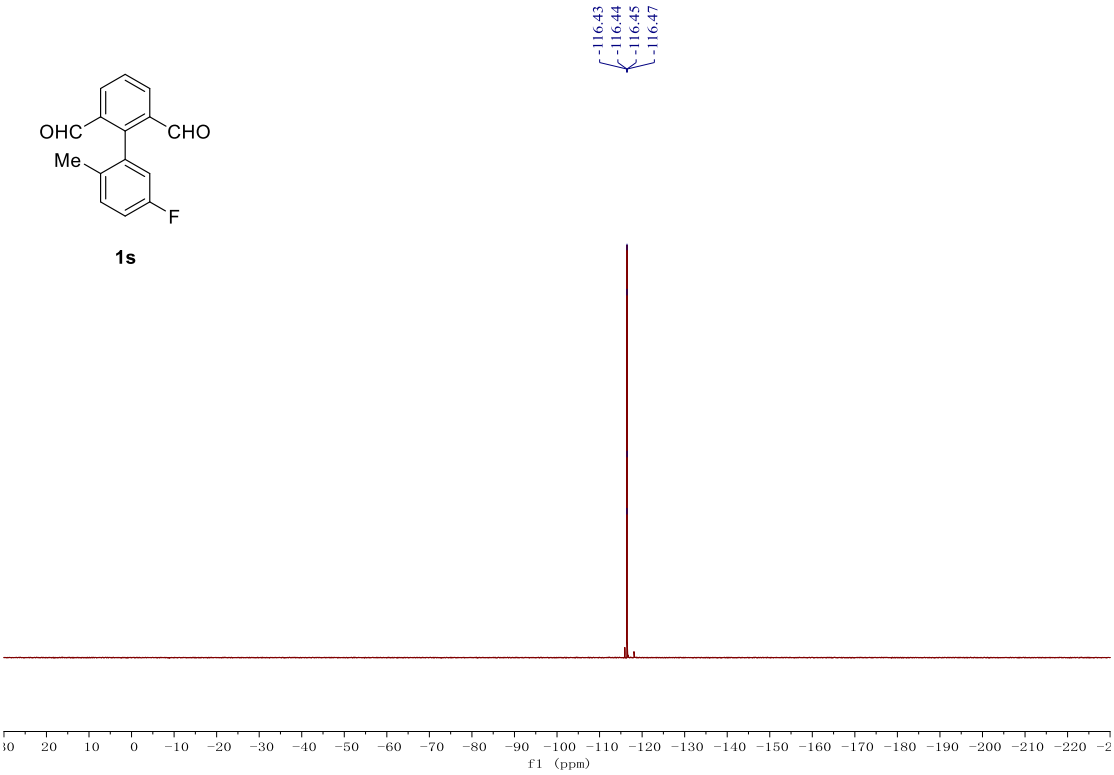
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1q.



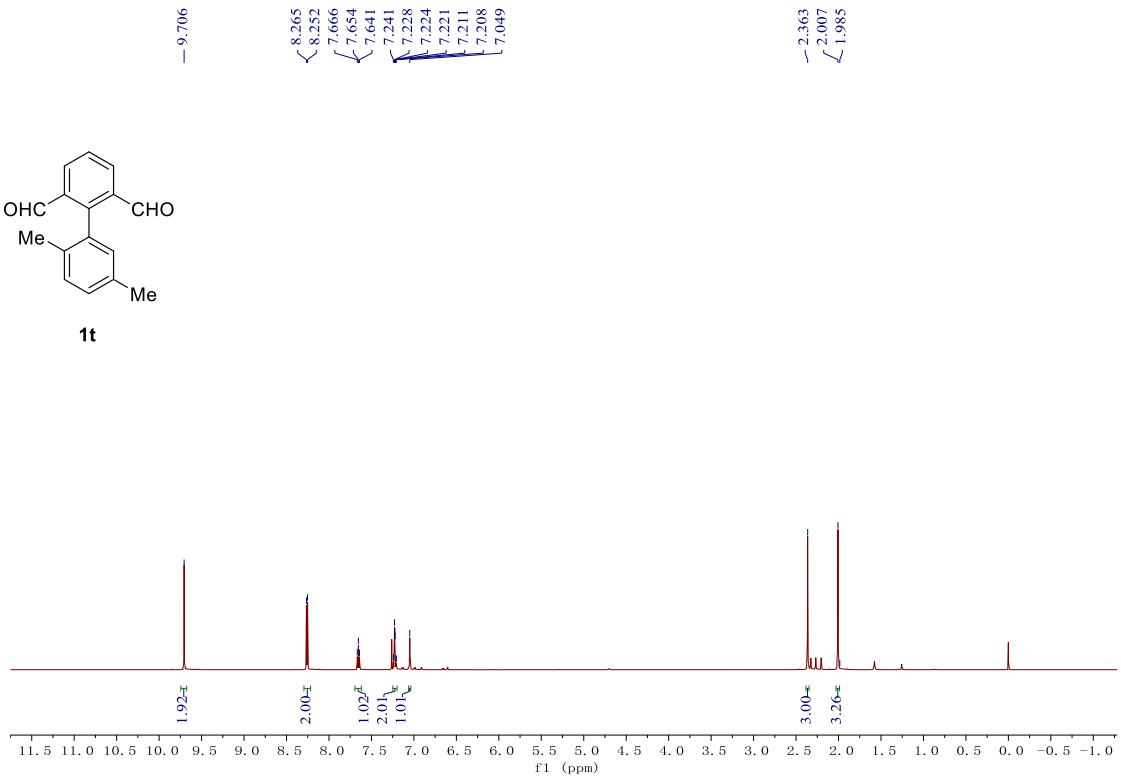
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1s.



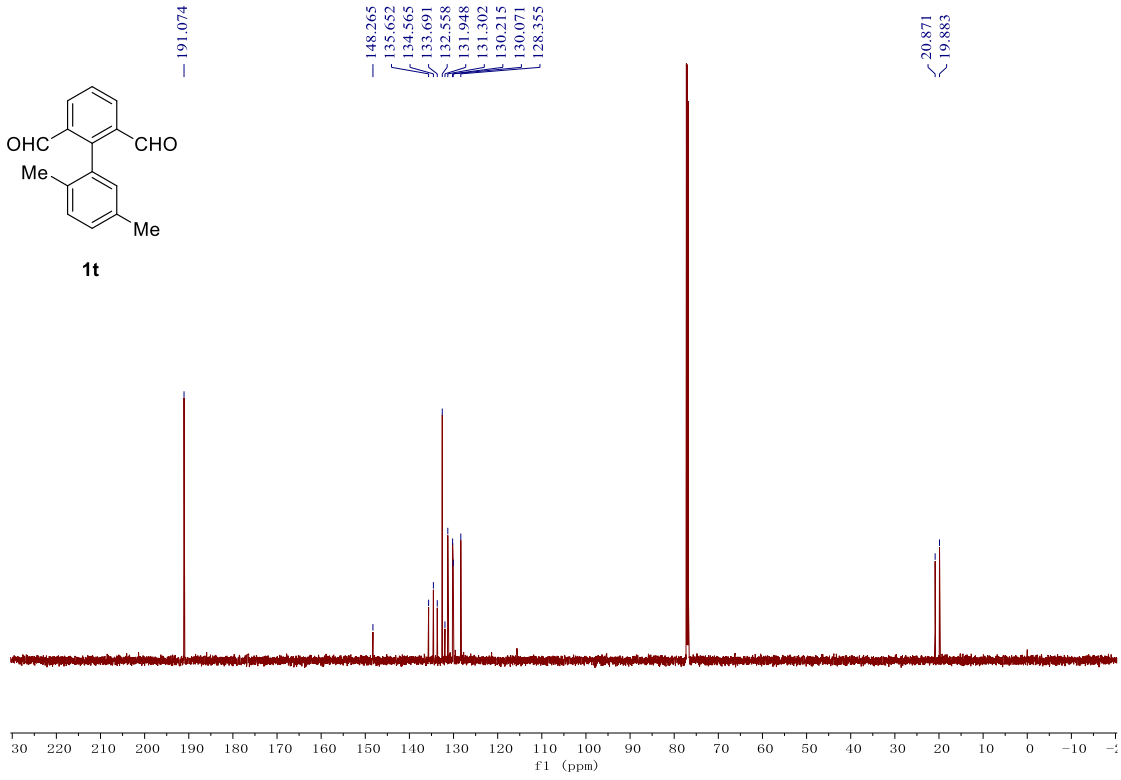
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1s.



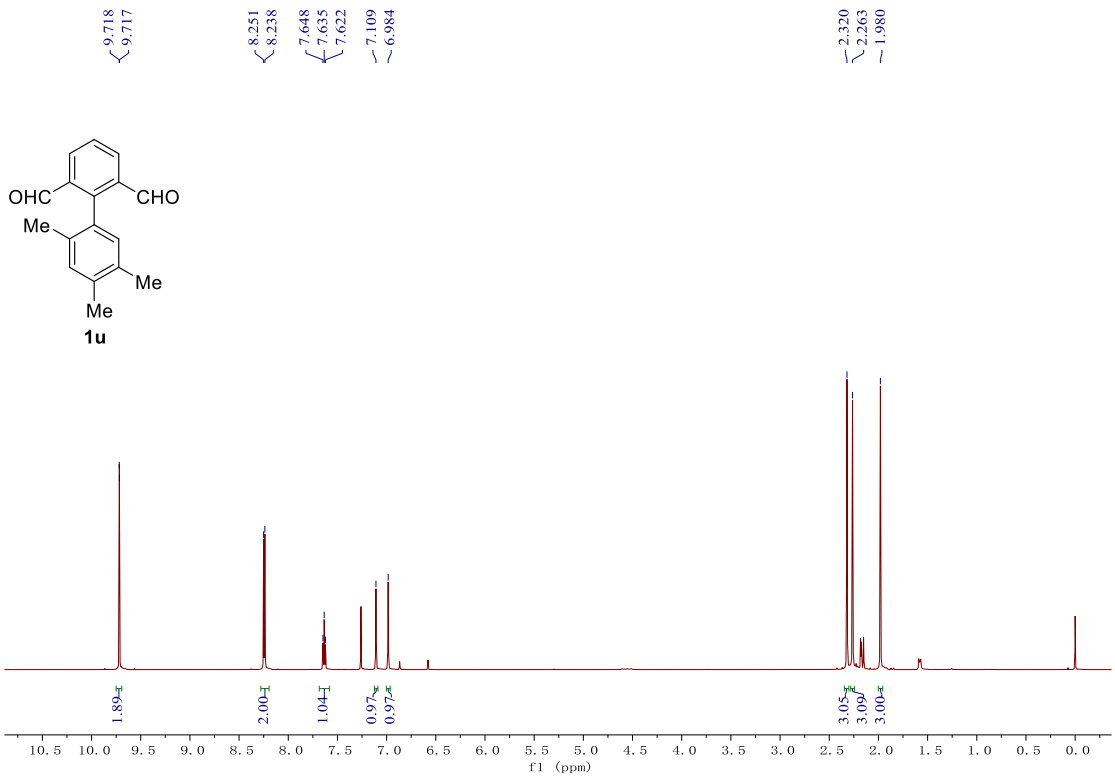
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 1s.



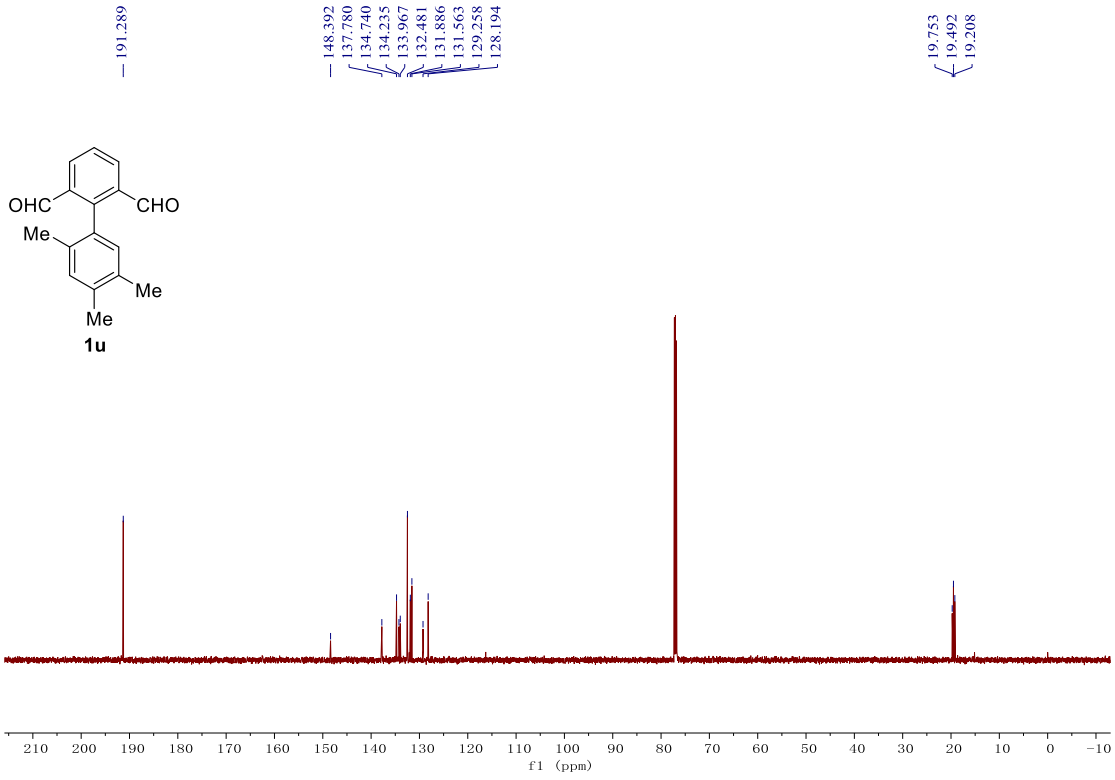
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1t.



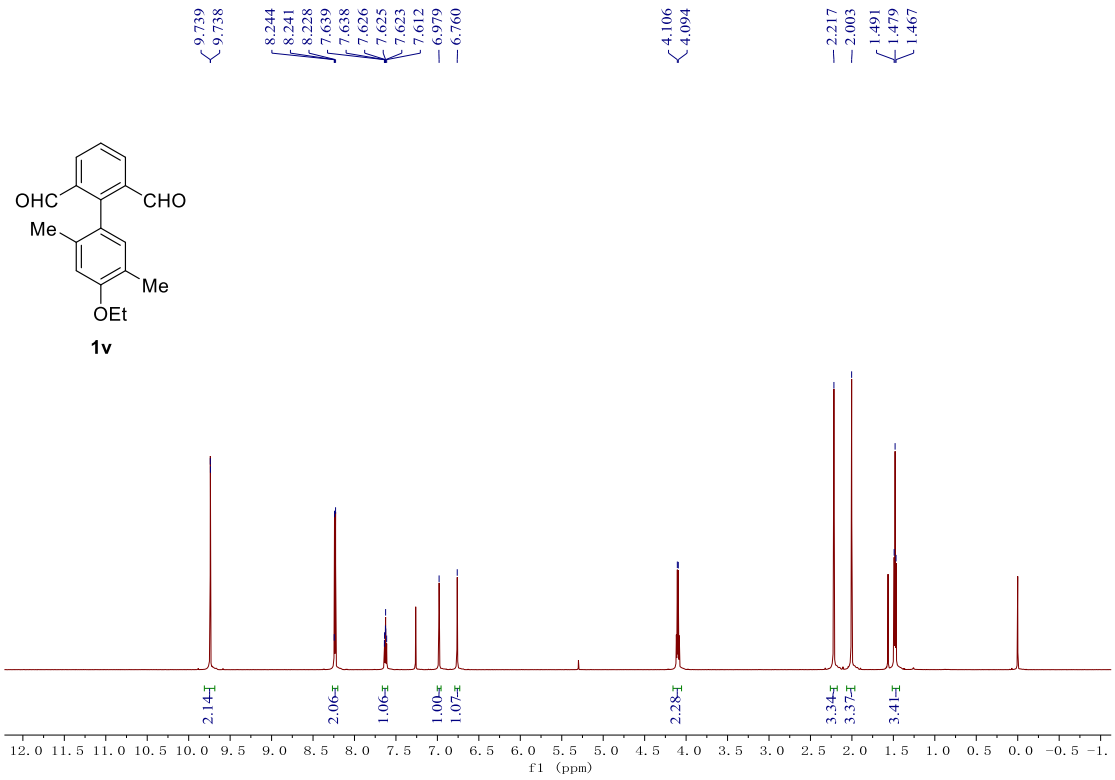
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1t.



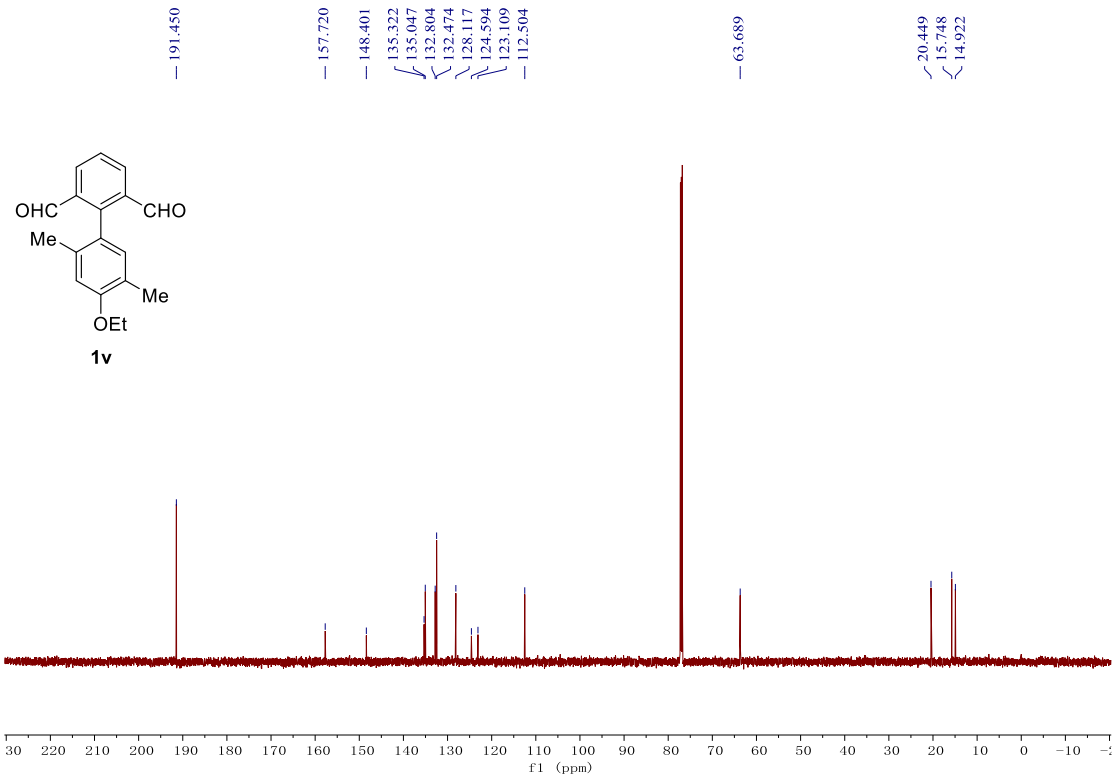
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1u.



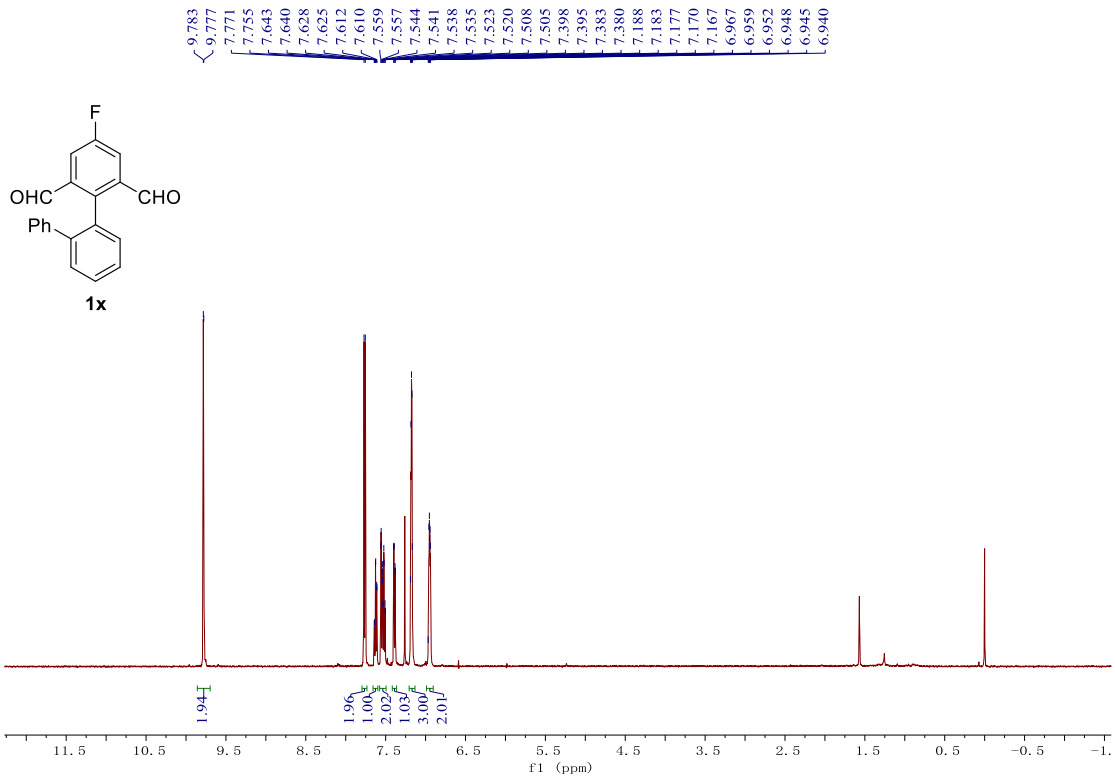
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1u.



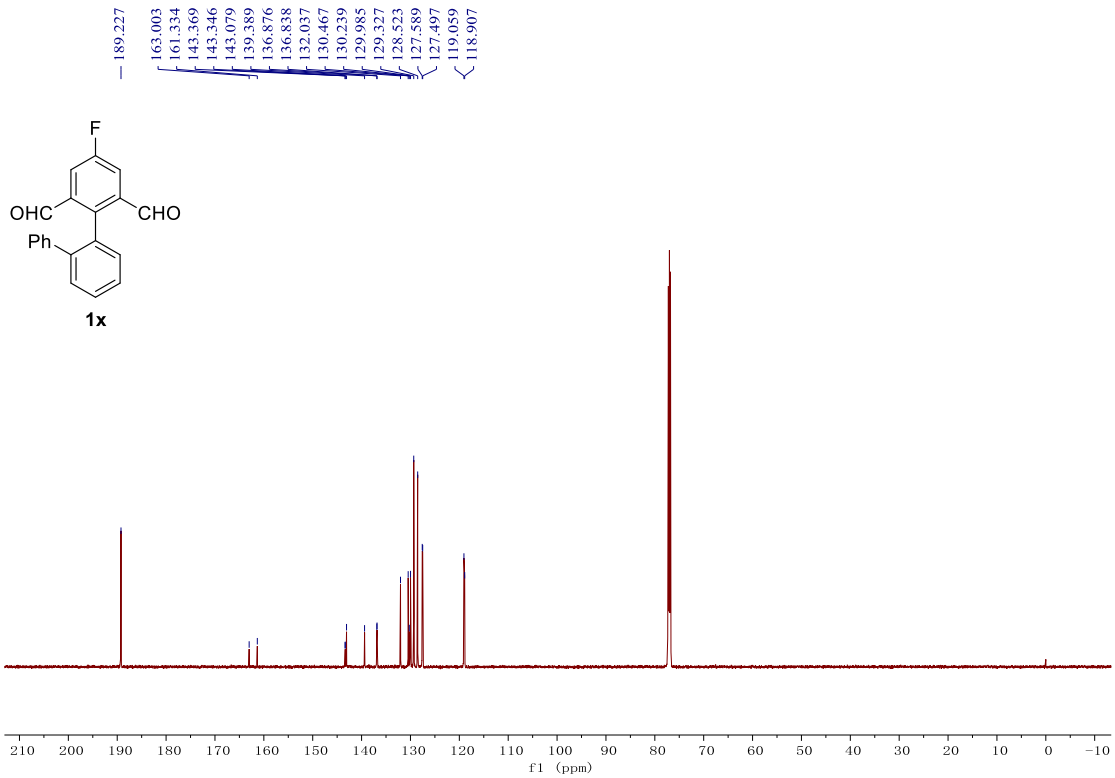
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1v.



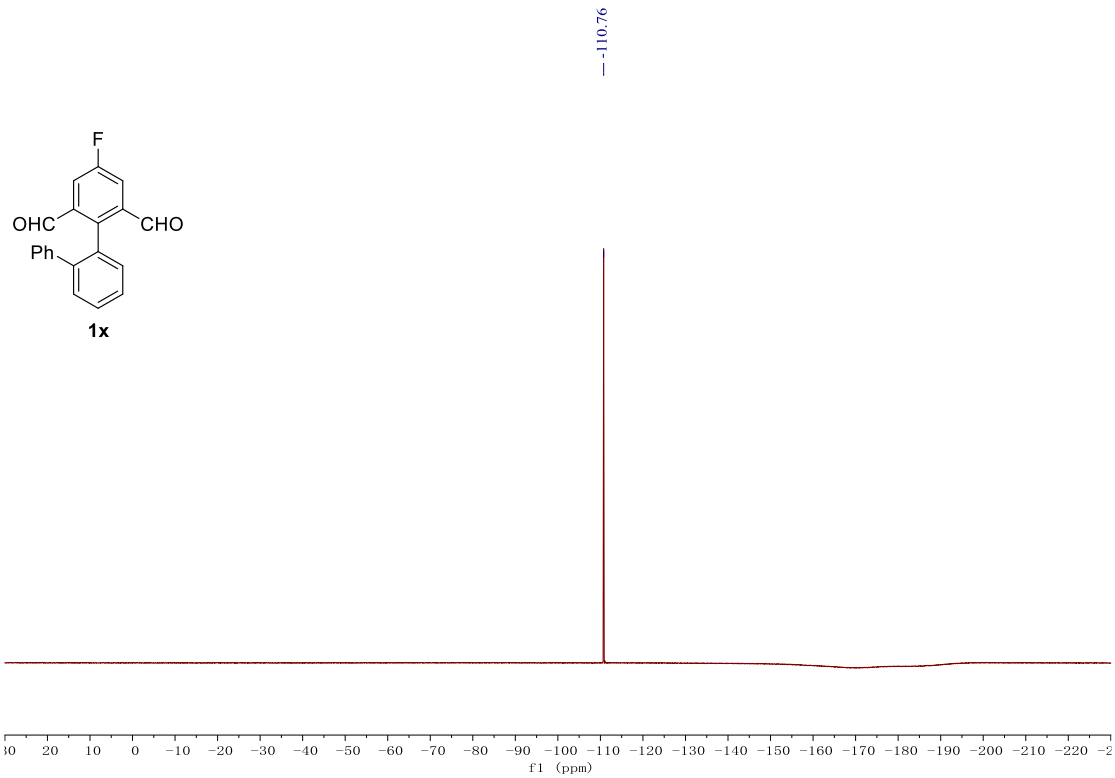
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1v.



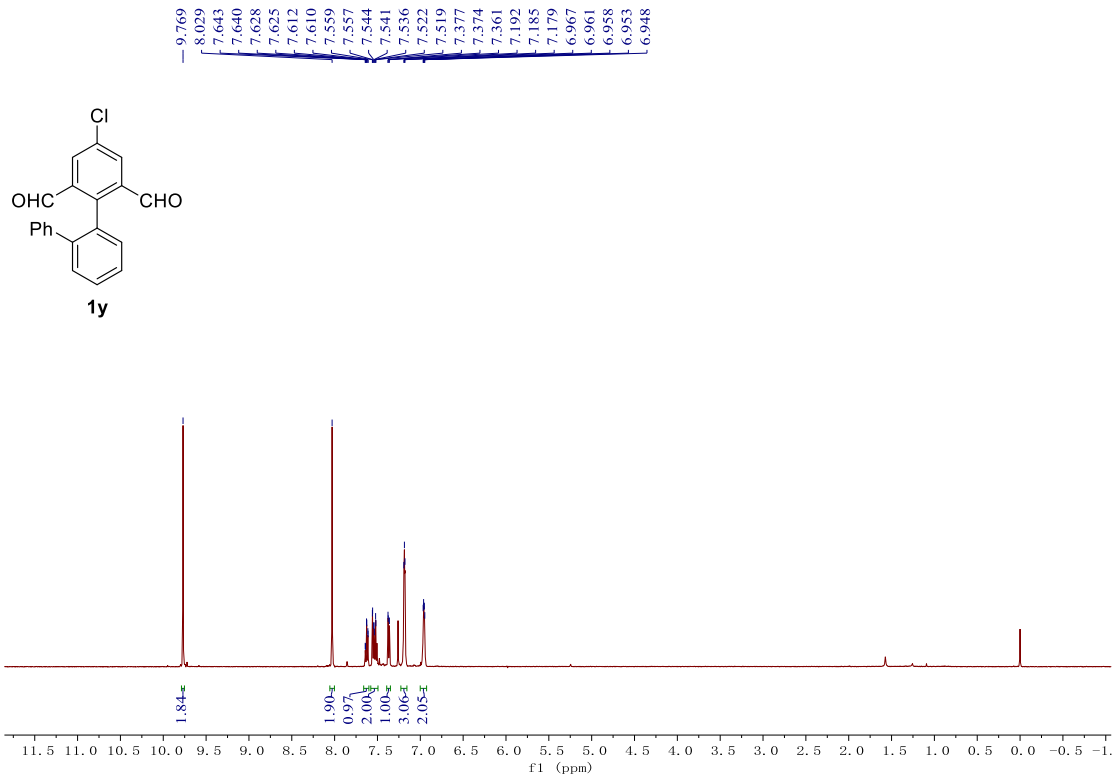
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1x.



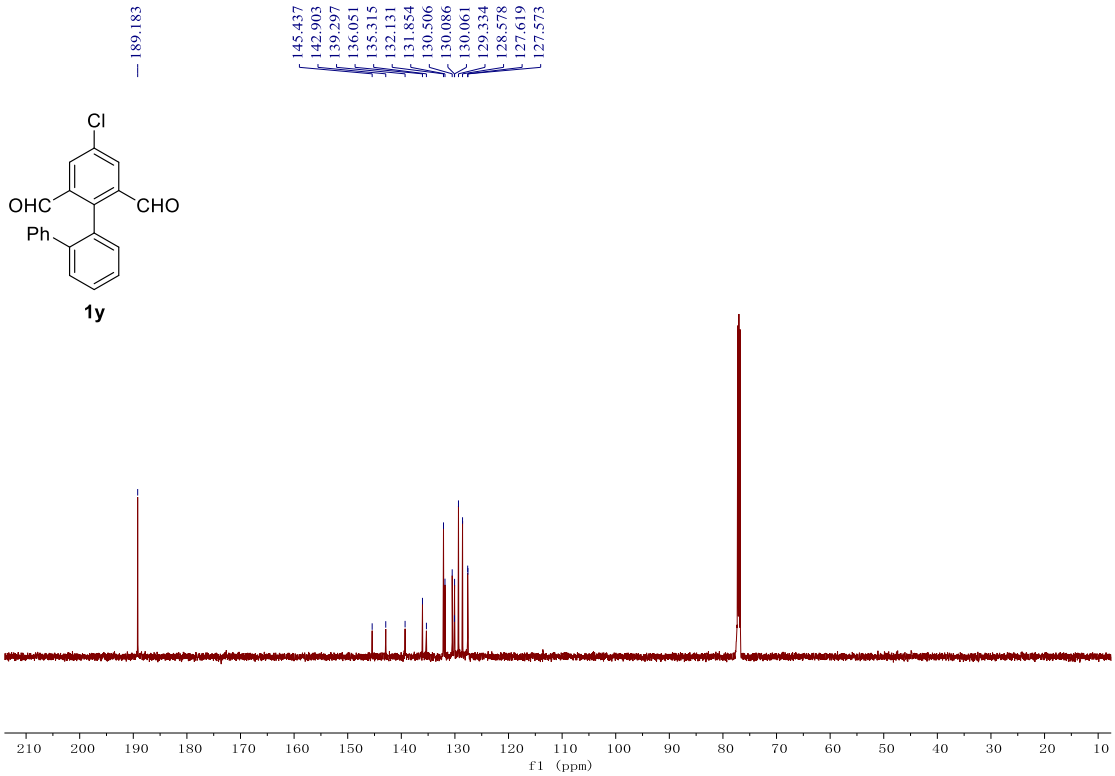
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1x.



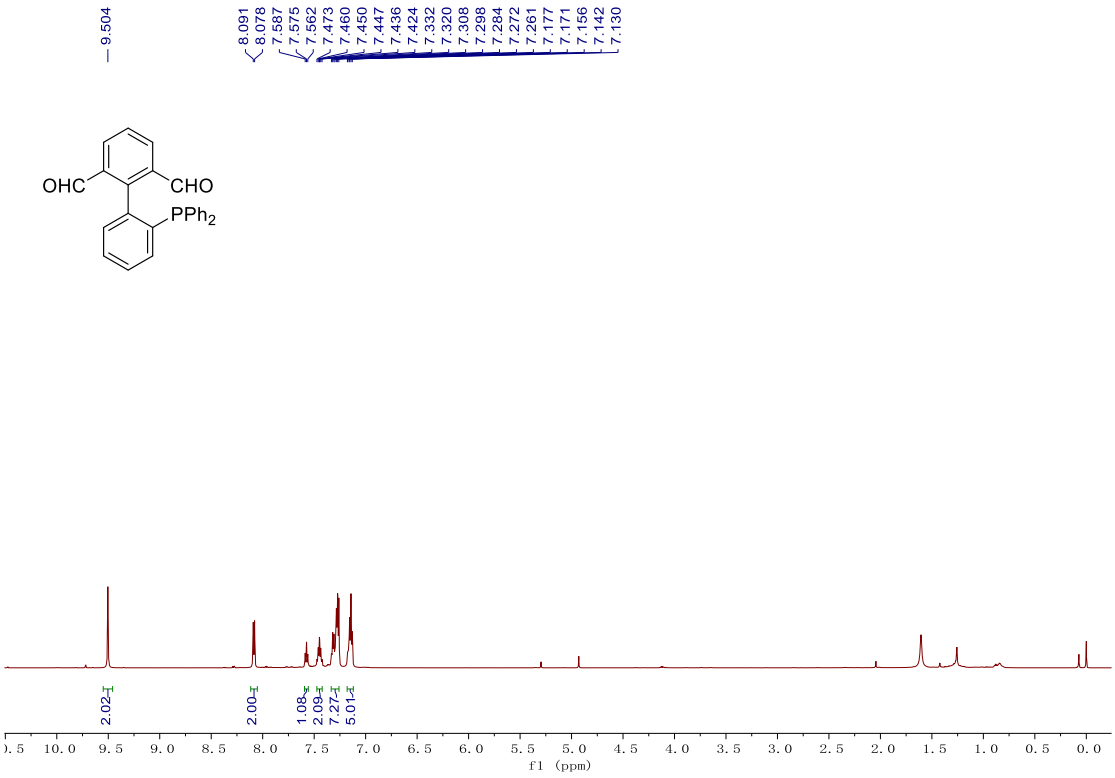
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of 1x.



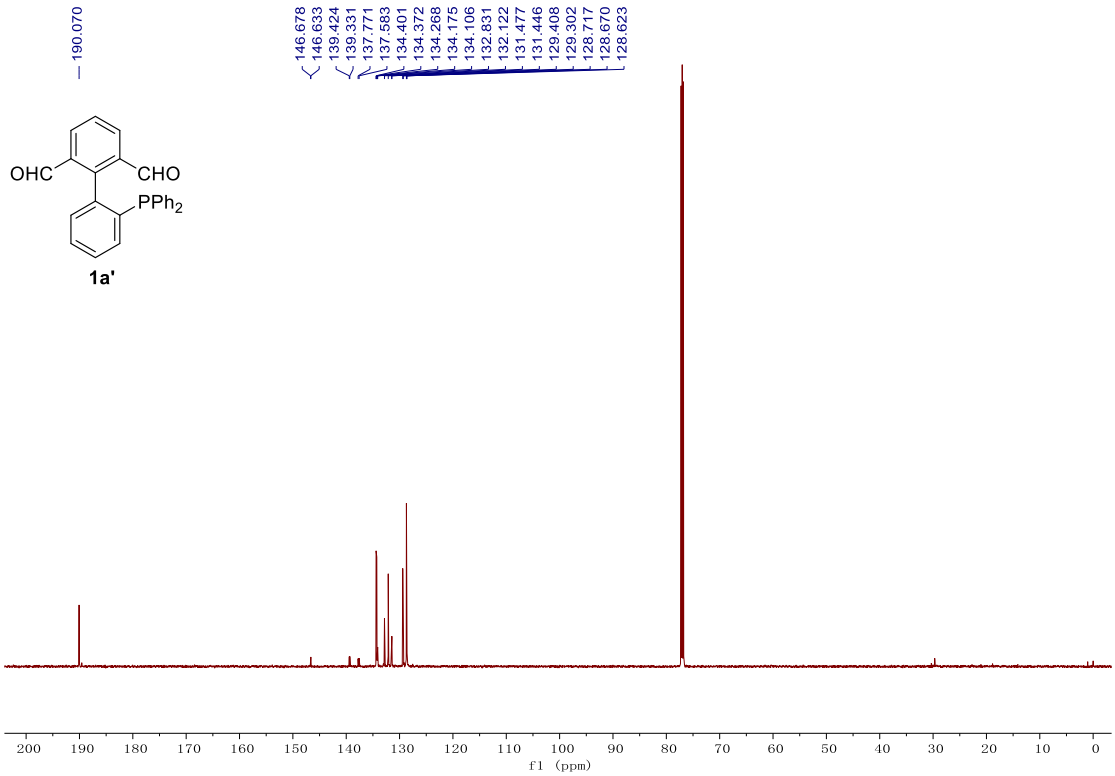
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of 1y.



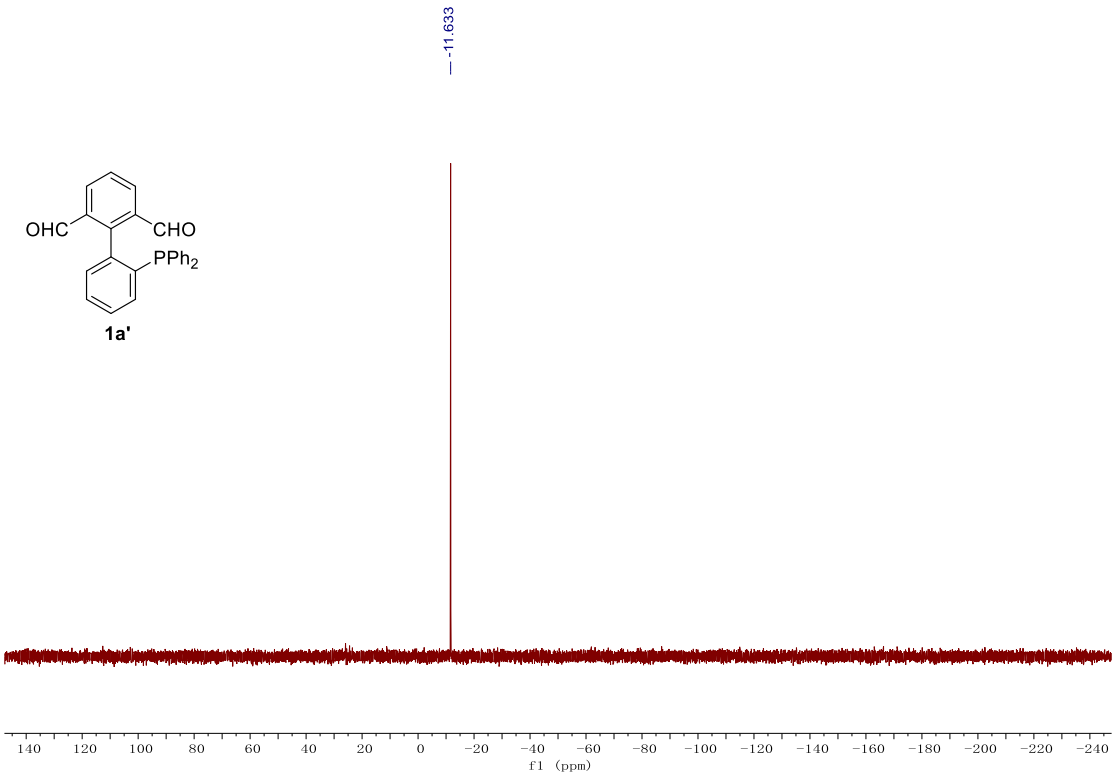
^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1y.



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 1a'.



^{13}C NMR (150 MHz, $CDCl_3$) spectrum of 1a'.



^{31}P NMR (243 MHz, Chloroform-*d*) spectrum of 1a'.